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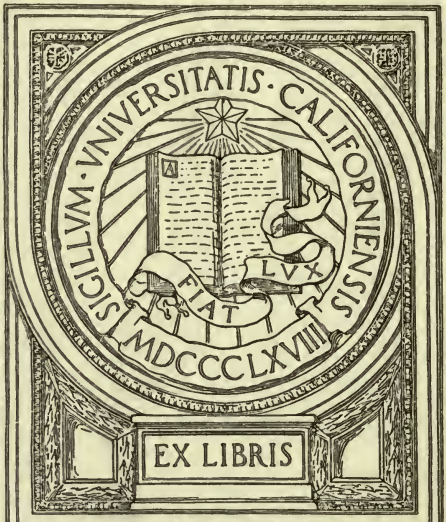

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A MANUAL

OF

ELEMENTARY CHEMISTRY,

THEORETICAL AND PRACTICAL.

BY

GEORGE FOWNES, F.R.S.,
LATE PROFESSOR OF PRACTICAL CHEMISTRY IN UNIVERSITY COLLEGE, LONDON

FROM THE

TENTH REVISED AND CORRECTED ENGLISH EDITION.

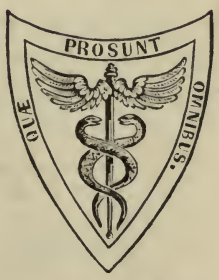
EDITED BY

ROBERT BRIDGES, M.D.,
PROFESSOR OF CHEMISTRY IN THE PHILADELPHIA COLLEGE OF PHARMACY.

California College of Pharmacy

WITH

ONE HUNDRED AND NINETY-SEVEN ILLUSTRATIONS.



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ADVERTISEMENT.

SO recent and so thorough has been the revision which this work has enjoyed at the hands of the English Editors, that but little has remained to be done in preparing the present reprint; while the enlargement which the volume has necessarily undergone, in the introduction of the most modern views and discoveries, has rendered it advisable to confine the additions to as moderate a compass as possible. The American Editor has therefore added but few notes, together with a number of illustrations, and has directed his attention rather to secure the accuracy so essential to a treatise of this nature. Especial care has been devoted to the formulæ, and errors have been corrected wherever a minute supervision has been able to detect them.

In its present enlarged and improved form, it is hoped that the work fairly represents the existing condition of the science, and that it may be found worthy a continuance of the very remarkable favor which it has so long enjoyed.

PHILADELPHIA, *May*, 1869.

41879

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TO

THE TENTH EDITION.

THE rapid progress of chemical discovery during the last few years has rendered it necessary to make considerable alterations and additions in almost every part of the present Edition.

The chapter on the General Principles of Chemical Philosophy has been re-written.

Some considerable additions have been made to the descriptions of the metals, especially those of rarer occurrence, several of which have acquired greatly increased importance by the more exact investigations of late years. The distinguishing reactions of the several metals are also given more fully than in former editions.

The greater part of the Organic Chemistry has been re-written, especially the sections relating to the Hydrocarbons, Alcohols, and Acids, upon which great light has been thrown by recent investigations.

The section on Animal Chemistry has been entirely revised.

The Atomic Weights used in this Edition are those which are now almost universally received among Chemists, and the Notation has been altered in accordance with them.

The Nomenclature has been simplified by discarding the word "of" in the names of salts, &c., using, for example, the term "silver nitrate" instead of "nitrate of silver."

The Weights and Measures used are those of the French decimal system; and Temperatures are expressed on the Centigrade scale, excepting where the contrary is expressly stated. A comparative Table of the two scales is given at the end of the volume.

H. Bence Jones.
Henry Watts.

London, *October*, 1868.

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TO

THE THIRD EDITION.

THE correction of this Edition for the Press was the daily occupation of Professor Fownes, until a few hours previous to his death in January, 1849.

His wish and his endeavor, as seen in his manuscript, were to render it as perfect and as minutely accurate as possible.

When he had finished the most important part of the Organic Chemistry, where the most additions were required, he told me he should "do no more," — he had "finished his work."

At his request I have corrected the Press throughout, and made a few alterations that appeared desirable in the only part which he had left unaltered, the Animal Chemistry.

The Index and the Press have also been corrected throughout by his friend Mr. Robert Murray.

H. Bence Jones, M.D.

30 Grosvenor Street, *Jan.*, 1850.

PREFACE

TO

THE FIRST EDITION.

THE design of the present volume is to offer to the student commencing the subject of Chemistry, in a compact and inexpensive form, an outline of the general principles of that science, and a history of the more important among the very numerous bodies which Chemical Investigations have made known to us. The work has no pretensions to be considered a complete treatise on the subject, but is intended to serve as an introduction to the larger and more comprehensive systematic works in our own language and in those of the Continent; and especially to prepare the student for the perusal of original memoirs, which, in conjunction with practical instruction in the laboratory, can alone afford a real acquaintance with the spirit of research and the resources of Chemical Science.

It has been my aim throughout to render the book as practical as possible, by detailing, at as great length as the general plan permitted, many of the working processes of the scientific laboratory, and by exhibiting, by the aid of numerous wood-engravings, the most useful forms of apparatus, with their adjustments and methods of use.

As one principal object was the production of a convenient and useful class-book for pupils attending my own lectures, I have been induced to adopt in the book the plan of arrangement followed in the lectures themselves, and to describe the non-metallic

elements and some of their most important compounds before discussing the subject of the general philosophy of Chemical Science, and even before describing the principle of the equivalent quantities, or explaining the use of the written symbolical language now universal among Chemists. For the benefit of those to whom these matters are already familiar, and to render the history of the compound bodies described in the earlier part of the work more complete, I have added in foot-notes the view adopted of their Chemical Constitution, expressed in symbols.

I have devoted as much space as could be afforded to the very important subject of Organic Chemistry; and it will, I believe, be found that there are but few substances of any general interest which have been altogether omitted, although the very great number of bodies to be described in a limited number of pages rendered it necessary to use as much brevity as possible.

GEO. FOWNES.

UNIVERSITY COLLEGE, LONDON.
October 5, 1847.

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MANUAL OF CHEMISTRY.

INTRODUCTION.

THE Science of Chemistry has for its object the study of the nature and properties of all the materials which enter into the composition or structure of the earth, the sea, and the air, and of the various organized or living beings which inhabit these latter. Every object accessible to man, or which may be handled and examined, is thus embraced by the wide circle of Chemical Science.

The highest efforts of Chemistry are constantly directed to the discovery of the general laws or rules which regulate the formation of chemical compounds, and determine the action of one substance upon another. These laws are deduced from careful observation and comparison of the properties and relations of vast numbers of individual substances; — and by this method alone. The science is entirely experimental, and all its conclusions the results of skilful and systematic experimental investigation.

The applications of the discoveries of Chemistry to the arts of life, and to the relief of human suffering in disease, are, in the present state of the science, both very numerous and very important, and encourage the hope of still greater benefits from more extended knowledge than that now enjoyed.

In ordinary scientific speech, the term *chemical* is applied to changes which permanently affect the properties or characters of bodies, in opposition to effects termed *physical*, which are not attended by such consequences. Changes of decomposition or combination are thus easily distinguished from those temporarily brought about by heat, electricity, magnetism, and the attractive forces, whose laws and effects lie within the province of Physics or Natural Philosophy.

Nearly all the objects presented by the visible world are of a compound nature, being chemical compounds, or variously disposed mixtures of chemical compounds, capable of being resolved into simpler forms of matter. Thus, a piece of limestone or marble, by the application of a red-heat, is decomposed into quicklime and a gaseous body, carbon dioxide. Both lime

and carbon dioxide are in their turn susceptible of decomposition, the former into a metal, calcium, and oxygen, and the latter into carbon and oxygen. For this purpose, however, simple heat does not suffice, the resolution of these substances into their components demanding the exertion of a high degree of chemical energy. Beyond this second step of decomposition the efforts of Chemistry have hitherto been found to fail; and the three bodies, calcium, carbon, and oxygen, having resisted all attempts to resolve them into simpler forms of matter, are accordingly admitted into the list of *elements*; — not from any belief in their real oneness of nature, but from the absence of any evidence that they contain more than one description of matter.

The partial study of certain branches of Physical Science, as the physical constitution of gases, the chief phenomena of heat and electricity, and a few other subjects, forms so indispensable an introduction to Chemistry itself, that it is rarely omitted in the usual courses of oral instruction. A sketch of these subjects is, in accordance with these views, placed at the commencement of the present volume.

PART I.—PHYSICS.

OF DENSITY AND SPECIFIC GRAVITY.

IT is of great importance at the outset to understand clearly what is meant by the terms *density* and *specific gravity*. By the *density of a body* is meant its *mass*, or *quantity of matter*, compared with the mass or quantity of matter of an *equal volume* of some standard body arbitrarily chosen. *Specific gravity* denotes the *weight* of a body, as compared with the weight of an equal bulk, or volume, of the standard body, which is reckoned as unity.* In all cases of solids and liquids, the standard of unity adopted in this country is pure water at the temperature of 15·5° C. (60° Fahr.) Anything else might have been chosen; there is nothing in water to render its adoption for the purpose mentioned indispensable: it is simply taken for the sake of convenience, being always at hand, and easily obtained in a state of perfect purity. An ordinary expression of specific weight, therefore, is a number explaining how many times the weight of an equal bulk of water is contained in the weight of the substance spoken of. If, for example, we say, that concentrated oil of vitriol has a specific gravity equal to 1·85, or that perfectly pure alcohol has a density of 0·794 at 15·5° C., we mean that equal bulks of these two liquids and of distilled water possess weights in the proportion of the numbers 1·85, 0·794, and 1; or 1850, 794, and 1000. It is necessary to be particular about the temperature, for, as will be hereafter shown, liquids are extremely expansible by heat; otherwise a constant bulk of the same liquid will not retain a constant weight. It will be proper to begin with the description of the mode in which the specific gravity of liquids is determined: this is the simplest case, and the one which best illustrates the general principle.

In order to obtain at pleasure the specific gravity of any particular liquid compared with that of water, it is only requisite to weigh equal bulks at the standard temperature, and then divide the weight of the liquid by the weight of the water; the quotient will of course be greater or less than unity, as the liquid experimented on is heavier or lighter than water. Now, to weigh equal bulks of two fluids, the simplest and best method is clearly to weigh them in succession in the same vessel, taking care that it is equally full on both occasions, a condition very easy of fulfilment.

A thin glass bottle, or flask, with a narrow neck, is procured, of the form represented below (fig. 1), and of such capacity as to contain, when filled to about half-way up the neck, exactly 1000 grains of distilled water at 15·5° C. Such a flask is readily procured from any one of the Italian

* In other words, density means comparative *mass*, and specific gravity comparative *weight*. These expressions, although really relating to distinct things, are often used quite indifferently in chemical writings, and without practical inconvenience, since mass and weight are directly proportional to each other.

artificers, to be found in every large town, who manufacture cheap thermometers for sale. A counterpoise of the exact weight of the empty bottle is made from a bit of brass, an old weight, or something of the kind, and carefully adjusted by filing. The bottle is then graduated, by introducing water at 15·5°, until it exactly balances the 1000-grain weight and counterpoise in the opposite scale; the height at which the water stands in the neck is marked by a scratch, and the instrument is complete for use. The liquid to be examined is brought to the temperature of 15·5°, and with it the bottle is filled up to the mark before mentioned; it is then weighed, the counterpoise being used as before, and the specific gravity directly ascertained.

Fig. 1.

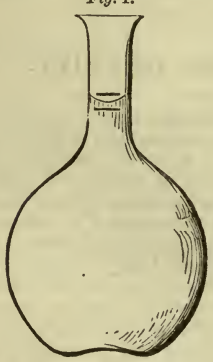
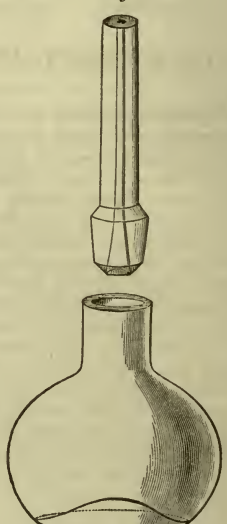


Fig. 2.



A watery liquid in a narrow glass tube always presents a curved surface, from the molecular action of the glass, the concavity being upwards. It is better, on this account, in graduating the bottle, to make two scratches, as represented in the figure, one at the top and the other at the bottom of the curve: this prevents any future mistake. The marks are easily made by a fine, sharp triangular file, the hard point of which, also, it may be observed, answers perfectly well for writing upon glass, in the absence of a proper diamond pencil.

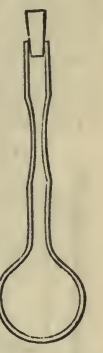
It will be quite obvious that the adoption of a flask holding exactly 1000 grains of water has no other object than to save the trouble of a very trifling calculation; any other quantity would answer just as well, and, in fact, the experimental chemist is often compelled to use a bottle of much smaller dimensions, from scarcity of the liquid to be examined.

When the specific gravity of a liquid is to be determined with great accuracy, a case which frequently occurs in chemical inquiries, a little glass bottle is used, of the form showed in fig. 2. This bottle is provided with a perforated conical glass stopper, most accurately fitted by grinding. By completely filling the little bottle with liquid, and carefully removing the portion of liquid which is displaced when the stopper is inserted, an unal-

terable measure is obtained. The least possible quantity of grease applied to the stopper greatly promotes the exact fitting.

When the chemist has only a small quantity of a fluid at his disposal, and wishes not to lose it, the little glass vessel (fig. 3) is particularly useful. It is formed by blowing a bubble on a glass tube. On that portion of the tube which is narrowed by drawing the tube out over a lamp, a fine scratch is made with a diamond. The bubble is filled up to this mark with a liquid whilst it stands in water the temperature of which is exactly known. A very fine funnel is used for filling the bubble, the stem of the funnel being drawn out so as to enter the tube, and the upper opening of the funnel being small enough to be closed by the finger. The glass stopper is only wanted as a guard, and does not require to fit perfectly.

Fig. 3.



The determination of the specific gravity of a solid body is made according to the same principles, and may be performed with the specific-gravity bottle (fig. 2). The bottle is first weighed full of water; the solid is then placed in the same pan of the balance, and its weight determined; finally, the solid is put into the bottle, displacing an equal bulk of water, the weight of which is determined by the loss on again weighing. Thus the weights of the solid and that of an equal bulk of water are obtained. The former divided by the latter gives the specific gravity.

For example, the weight of a small piece of silver wire was found to be . . . . . 98·18 grains.
Glass bottle filled with water . . . . . 294·69 "

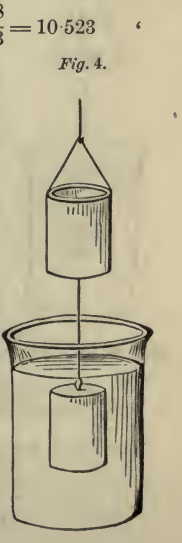
392·87 "

After an equal volume of water was displaced by the silver, the weight was . . . . . 383·54 "

Hence the displaced water weighed . . . . . 9·33 "
From this, the specific gravity of the silver wire . . . . . $\left\{\frac{98\cdot18}{9\cdot33}\right. = 10\cdot523$

Another highly ingenious, but less exact method of determining the specific gravity of solids, is based on the well-known theorem of Archimedes.

Fig. 4.



This theorem may be thus expressed:

> When a solid is immersed in a fluid, it loses a portion of its weight; and this portion is equal to the weight of the fluid which it displaces; that is, to the weight of its own bulk of that fluid.

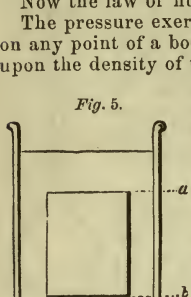
It is easy to give experimental proof of this very important proposition, as well as to establish it by reasoning. Figure 4 represents a little apparatus for the former purpose. This consists of a thin cylindrical vessel of brass, into the interior of which fits very accurately a solid cylinder of the same metal, thus exactly filling it. When the cylinder is suspended beneath the bucket, as seen in the sketch, the whole hung from the arm of a balance and counterpoised, and then the cylinder itself immersed in water, it will be found to have lost a certain weight; and that this loss is precisely equal to the weight of an equal bulk of water, may then be proved by filling the bucket to the brim, whereupon the equilibrium will be restored.

The consideration of the great hydrostatic law of fluid pressure easily proves the truth of the principle laid down. Let the reader figure to himself a vessel of water, having immersed in it a solid cylindrical or rectangular body, and so adjusted with respect to density, that it shall float indifferently in any part beneath the surface (fig. 5.)

Now the law of fluid pressure is to this effect:

The pressure exerted by a fluid on any point of the containing vessel, or on any point of a body immersed beneath its surface, is dependent, firstly, upon the density of the fluid, and, secondly, upon the vertical depth of the point in question below the surface. It is independent of the form and lateral dimensions of the vessel or immersed body. Moreover, owing to the peculiar physical constitution of fluids, this pressure is exerted in every direction, upward, downward, and laterally, with equal force.

Fig. 5.



The floating body is in a state of equilibrium; therefore the pressure downward caused by its gravitation must be exactly compensated by the upward transmitted pressure of the column of water *a*, *b*. But this pressure downward is obviously equal to the weight of an equal quantity of water, since the body of necessity displaces its own bulk. Hence the weight which a body loses when immersed in, or floated on water, is equal to the weight of the volume of water displaced by that body.

Whatever be the density of the substance, it will be buoyed up to this amount: in the case supposed, the buoyancy is equal to the whole weight of the body, which is thus, while in the water, reduced to nothing.

Fig. 6.

A little reflection will show that the same reasoning may be applied to a body of irregular form; besides, a solid of any figure may be divided by the imagination into a multitude of little perpendicular prisms or cylinders, to each of which the argument may be applied. What is true of each individually must necessarily be true of the whole together.

This is the fundamental principle; its application is made in the following manner:—Let it be required, for example, to know the specific gravity of a body of extremely irregular form, as a small group of rock crystals: the first part of the operation consists in determining its absolute weight, or, more correctly speaking, its weight in air; it is next suspended from the balance-pan by a fine horsehair, immersed completely in pure water at 15·5°, and again weighed. It now weighs less, the difference being the weight of the water it displaces, that is, the weight of an equal bulk. This being known, nothing more is required than to find, by division, how many times the latter number is contained in the former; the quotient will be the density, water, at the temperature of 15·5°, being taken = 1. For example:

The quartz-crystals weigh in air	293·7 grains.
When immersed in water, they weigh	180·1 "
Difference, being the weight of an equal volume of water	113·6 "

$$\frac{293{\cdot}7}{113{\cdot}6} = 2{\cdot}59,$$ the specific gravity required.

The rule is generally thus written: "Divide the weight in air by the loss of weight in water, and the quotient will be the specific gravity." In reality it is not the weight in air which is required, but the weight the body would have in empty space: the error introduced, namely, the weight of an equal bulk of air is so trifling, that it is usually neglected.

Fig. 7.

Sometimes the body to be examined is lighter than water, and floats. In this case, it is first weighed, and afterwards attached to a piece of metal heavy enough to sink it, and suspended from the balance. The whole is then exactly weighed, immersed in water, and again weighed. The difference between the two weighings gives the weight of a quantity of water equal in bulk to both together. The light substance is then detached, and the same operation of weighing in air, and again in water, repeated on the piece of metal. These data give the means of finding the specific gravity, as will be at once seen by the following example:

Light substance (a piece of wax) weighs in air . .	133·7 grains.
Attached to a piece of brass, the whole now weighs .	183·7 "
Immersed in water, the system weighs	38·8 "
Weight of water equal in bulk to brass and wax . .	144·9 "
Weight of brass in air	50·0 "
Weight of brass in water	44·4 "
Weight of equal bulk of water	5·6 "
Bulk of water equal to wax and brass	144·9 "
Bulk of water equal to brass alone	5·6 "
Bulk of water equal to wax alone	139·3 "

$$\frac{133{\cdot}7}{139{\cdot}3} = 0{\cdot}9598$$

In all such experiments it is necessary to pay attention to the temperature and purity of the water, and to remove with great care all adhering air-bubbles,* otherwise a false result will be obtained.

Other cases require mention in which these operations must be modified to meet particular difficulties. One of these happens when the substance is dissolved or acted upon by water. The difficulty is easily overcome by substituting some other liquid of known density which experience shows is without action. Alcohol or oil of turpentine may generally be used when water is inadmissible. Suppose, for instance, the specific gravity of crystallized sugar is required, we proceed in the following way: The specific gravity of the oil of turpentine is first carefully determined; let it be 0·87; the sugar is next weighed in the air, then suspended by a horsehair, and weighed in the oil; the difference is the weight of an equal bulk of the latter; a simple calculation gives the weight of a corresponding volume of water: —

* A simple plan of avoiding altogether the adhesion of air-bubbles, which often are not easily perceived, consists in heating the water to ebullition, introducing the body which has been weighed in the air into the still boiling water, which is then allowed to cool to 15·5°, when the second weighing is performed.

Weight of sugar in air	400 grains.
Weight of sugar in oil of turpentine	182·5 "
Weight of equal bulk of oil of turpentine . . .	217·5 "

$$87 : 100 = 217{\cdot}5 : 250,$$

the weight of an equal bulk of water; hence the specific gravity of the sugar,—

$$\frac{400}{250} = 1{\cdot}6.$$

If the substance to be examined consists of small pieces, or of powder, then the method first described, namely, that of the specific-gravity bottle, can alone be used.

By this method the specific gravities of metals in powder, metallic oxides, and other compounds, and salts of all descriptions, may be determined with great ease. Oil of turpentine may be used with most soluble salts. The crystals should be crushed or roughly powdered to avoid errors arising from cavities in their substance.

The specific gravity of a solid can also be readily found by immersing it in a transparent liquid, the density of which has been so adjusted that the solid body remains indifferently at whatever depth it may be placed. The specific gravity of the liquid must now be determined, and it will, of course, be the same as that of the solid. It is necessary that the liquid chosen for this experiment do not dissolve or in any way act upon the solid. Solutions of mercuric nitrate, or corrosive sublimate, can be used for bodies heavier than water, while certain oils, and essences, and mixtures of alcohol and water, can be conveniently employed for such substances as have a lower specific gravity than water. This method is not only adapted to the exact determination of specific gravities, but also serves in many cases as a means of readily distinguishing substances much resembling one another. Suppose, for instance, a solution of mercuric nitrate to have a specific gravity 3; a red amethyst (2·67) will then float upon, and a topaz of the same color (3·55) will sink in this liquid.

Fig. 8.

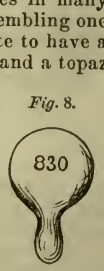
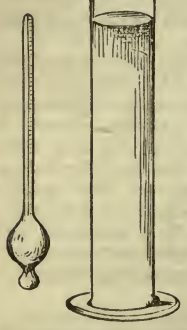


Fig. 9.



The theorem of Archimedes affords the key to the general doctrine of the equilibrium of floating bodies, of which an application is made in the common hydrometer,—an instrument for finding the specific gravities of liquids in a very easy and expeditious manner.

When a solid body is placed upon the surface of a liquid specifically heavier than itself, it sinks down until it displaces a quantity of liquid equal to its own weight, at which point it floats. Thus, in the case of a substance floating in water, whose specific weight is one half that of the liquid, the position of equilibrium will involve the immersion of one half of the body, inasmuch as its whole weight is counterpoised by a quantity of water equal to half its volume. If the same body were put into a liquid of one half the specific gravity of water, if such could be found, it would then sink beneath the surface, and remain indifferently in any part. A floating body of known specific gravity may thus be used as an indicator of the specific gravity of a liquid. In this manner little glass beads (fig. 8) of known specific gravities are sometimes employed in the arts to ascertain in a rude manner the specific

gravity of liquids; the one that floats indifferently beneath the surface, without either sinking or rising, has of course the same specific gravity as the liquid itself; this is pointed out by the number marked upon the bead.

The hydrometer (fig. 9) in general use consists of a floating vessel of thin metal or glass, having a weight beneath to maintain it in an upright position, and a stem above bearing a divided scale. The use of the instrument is very simple. The liquid to be tried is put into a small narrow jar, and the instrument floated in it. It is obvious that the denser the liquid, the higher will the hydrometer float, because a smaller displacement of liquid will counterbalance its weight. For the same reason, in a liquid of less density, it sinks deeper. The hydrometer comes to rest almost immediately, and then the mark on the stem at the fluid-level may be read off.

Very extensive use is made of instruments of this kind in the arts; they sometimes bear different names, according to the kind of liquid for which they are intended; but the principle is the same in all. The graduation is very commonly arbitrary, two or three different scales being unfortunately used. These may be sometimes reduced, however, to the true numbers expressing the specific gravity by the aid of tables of comparison drawn up for the purpose. (*See* APPENDIX.)

Tables are likewise used to reduce the readings of the hydrometer at any temperature to those of the normal temperature.

The division of the instrument from below, upward, into 100 parts, is much to be preferred to these arbitrary scales. Half of these divisions must be made upon the stem. The 100th division indicates the point of immersion in distilled water at 15·5° C. (60° Fahr.) If in another liquid the instrument sinks less deeply, for example to 60, then 60 volumes of this liquid weigh as much as 100 volumes of water. Hence the weight of 100 volumes, that is, the specific gravity, is $\frac{100}{60} = 1{\cdot}67$. By this arrangement of the scale, it is evident that the reduction of the specific gravity is so simple that no tables are required.

A very convenient and useful instrument in the shape of a small hydrometer, for taking the specific gravity of urine, has been put into the hands of the physician;* it may be packed into a pocket-case, with a little jar and a thermometer, and is always ready for use.†

Fig. 10.

Fig. 11.

[* The graduation of the urinometer is such that each degree represents 1-1000, thus giving the actual specific gravity without calculation, for the number of degrees on the scale cut by the surface of the liquid when this instrument is at rest, added to 1000, will represent the density of the liquid. If, for example, the surface of the liquid coincide with 13 on the scale, the specific gravity will be 1013, about the average density of healthy urine. — R. B.]

[† The mode of determining the specific gravity of a liquid by means of a solid has been omitted

The determination of the specific gravity of gases and vapors of volatile liquids is a problem of very great practical importance to the chemist: the theory of the operation is as simple as when liquids themselves are concerned, but the processes are much more delicate, and involve besides certain corrections for differences of temperature and pressure, founded on principles yet to be discussed. It will be proper to defer the considerations of these matters for the present. The method of determining the specific gravity of a gas will be found described under the head of Oxygen, and that of the vapor of a volatile liquid in the Introduction to Organic Chemistry.

in the text. It results from the theorem of Archimedes, that if any solid be immersed in water and then in any other liquid, the loss of weight sustained in each case will give the relative weights of equal bulks of the liquids, and on dividing the weight of the liquid by the weight of the water, the quotient will be the specific gravity of the liquid experimented on. For instance, let a piece of glass rod (fig. 10) be suspended from the balance pan and exactly counterpoised, then immerse it in water and restore the equipoise by weights added to the pan to which the glass is suspended, the amount will give the loss of weight by immersion or the weight of a bulk of water equal to that of the stopper. Now wipe the glass dry, and having removed the additional weights, immerse it in the other liquid, and restore the equipoise as before; this latter weight is the weight of a bulk of the liquid equal to that of the water. The latter divided by the former gives the specific gravity. For example:—

The glass stopper loses by immersion in water	171 grains.
The glass stopper loses by immersion in alcohol	143 "

$\frac{143}{171} = .836$, the specific gravity required. — R. B.]

OF THE PHYSICAL CONSTITUTION OF THE ATMOSPHERE AND OF GASES IN GENERAL.

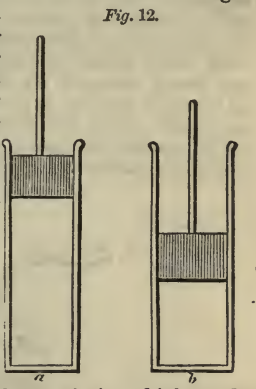
IT requires some little abstraction of mind to realize completely the condition in which all things at the surface of the earth exist. We live at the bottom of an immense ocean of gaseous matter, which envelops everything, and presses upon everything with a force which appears, at first sight, perfectly incredible, but whose actual amount admits of easy proof.

Gravity being, so far as is known, common to all matter, it is natural to expect that gases, being material substances, should be acted upon by the earth's attraction, as well as solids and liquids. This is really the case, and the result is the weight or pressure of the atmosphere, which is nothing more than the effect of the attraction of the earth on the particles of air.

Before describing the leading phenomena of the atmospheric pressure, it is necessary to notice one very remarkable feature in the physical constitution of gases, upon which depends the principle of an extremely valuable instrument, the air-pump.

Gases are in the highest degree elastic; the volume or space which a gas occupies depends upon the pressure exerted upon it. Let the reader imagine a cylinder, *a*, closed at the bottom, in which moves a piston, air-tight, so that no air can escape between the piston and the cylinder. Suppose now the piston be pressed downward with a certain force; the air beneath it will be compressed into a smaller bulk, the amount of this compression depending on the force applied; if the power be sufficient, the bulk of the gas may be thus diminished to one hundredth part or less. When the pressure is removed, the elasticity or *tension*, as it is called, of the included air or gas, will immediately force up the piston until it arrives at its first position.

Fig. 12.

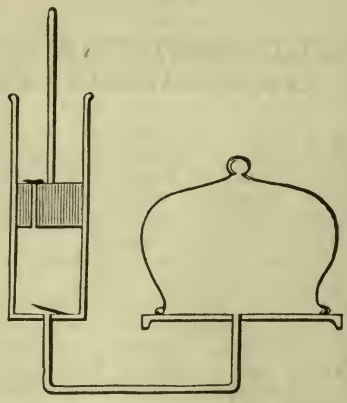


Again, take fig. 12, *b*, and suppose the piston to stand about the middle of the cylinder, having air beneath in its usual state. If the piston be now drawn upward, the air below will expand, so as to fill completely the increased space, and this to an apparently unlimited extent. A volume of air, which, under ordinary circumstances, occupies the bulk of a cubic inch, might, by the removal of the pressure upon it, be made to expand to the capacity of a whole room, while a renewal of the former pressure would be attended by a shrinking down of the air to its former bulk. The smallest portion of gas introduced into a large exhausted vessel becomes at once diffused through the whole space, an equal quantity being present in every part; the vessel is *full*, although the gas is in a state of extreme tenuity. This power of expansion which air possesses may have, and probably has, in reality, a limit; but the limit is never reached in practice. We are quite safe in the assumption that for all purposes of experiment, however refined, air is perfectly elastic.

It is usual to assign a reason for this indefinite expansibility by ascribing

to the particles of material bodies, when a in gaseous state, a self-repulsive agency. This statement is commonly made somewhat in this manner:

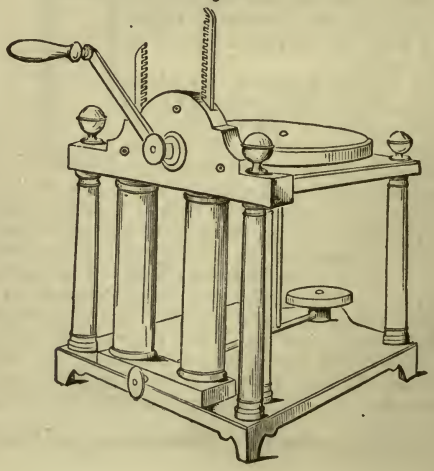
Fig. 13.



matter is under the influence of two opposite forces, one of which tends to draw the particles together, the other to separate them. By the preponderance of one or other of these forces, we have the three states called solid, liquid, and gaseous. When the particles of matter, in consequence of the direction and strength of their mutual attractions, possess only a very slight power of motion, a solid substance results; when the forces are nearly balanced, we have a liquid, the particles of which in the interior of the mass are free to move, but yet to a certain extent are held together; and lastly, when the attractive power seems to be completely overcome by its antagonist, we have a gas or vapor.

Various names are applied to these forces, and various ideas entertained

Fig. 14.



concerning them: the attractive forces bear the name of cohesion when they are exerted between particles of matter separated by an immeasurably small interval, and gravitation when the distance is great. The repulsive principle is often thought to be identical with the principle of heat. We shall return to this subject in discussing the nature of heat. (*See* page 77.)

The ordinary air-pump, shown in section in fig. 13, consists essentially of a metallic cylinder, in which moves a tightly fitting piston, by the aid of its rod. The bottom of the cylinder communicates with the vessel to be exhausted, and is furnished with a valve opening upward. A similar valve, also opening upward, is fitted to the piston: these valves are made with slips of oiled silk. When the piston is raised from the bottom of the cylinder, the space left beneath it must be void of air, since the piston-valve opens only in one direction; the air within the receiver having on that side nothing to oppose its elastic power but the weight of the little valve, lifts the latter, and escapes into the cylinder. So soon as the piston begins to descend, the lower valve closes, by its own weight, or by the transmitted pressure from above, and communication with the receiver is cut off. As the descent of the piston continues, the air inclosed in the cylinder becomes compressed, its elasticity is increased, and at length it forces open the upper valve, and escapes into the atmosphere. In this manner, a cylinder full of air is at every stroke of the pump removed from the receiver. During the descent of the piston, the upper valve remains open, and the lower closed, and the reverse during the opposite movement.

In practice, it is very convenient to have two such barrels or cylinders, arranged side by side, the piston-rods of which are formed into racks, having a pinion, or small-toothed wheel, between them, moved by a winch. By this contrivance the operation of exhaustion is much facilitated and the labor lessened. The arrangement is shown in fig. 14, on the preceding page.

A simpler form of air-pump is thus constructed: the cylinder, which may be of large dimensions, is furnished with an accurately fitted solid piston, the rod of which moves, air-tight, through a contrivance called a stuffing-box, at the top of the cylinder, where also the only valve *essential* to the apparatus is to be found: the latter is a solid conical plug of metal, shown at *a* in the figure, kept tight by the oil contained in the chamber into which it opens. The communication with the vessel to be exhausted is made by a tube which enters the cylinder a little above the bottom. The action is the following: let the piston be supposed in the act of rising from the bottom of the cylinder; as soon as it passes the mouth of the tube *t*, all communication is stopped between the air above the piston and the vessel to be exhausted; the inclosed air suffers compression until it acquires sufficient elasticity to lift the metal valve and escape by bubbling through the oil. When the piston makes its descent, and this valve closes, a vacuum is left in the upper part of the cylinder, into which the air in the receiver rushes so soon as the piston has passed below the orifice of the connecting tube.

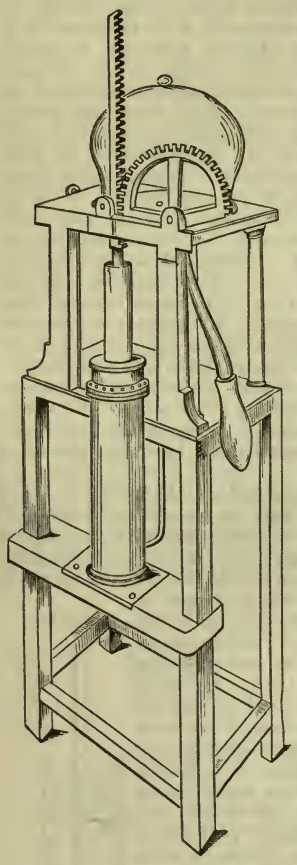
Fig. 15.

In the silk-valved air-pump, exhaustion ceases when the elasticity of the air in the receiver becomes too feeble to raise the valve: in that last described the exhaustion may, on the contrary, be carried to an indefinite extent, without, however, under the most favorable circumstances, becoming complete. The conical valve is made to project a little below the cover of the cylinder, so as to be forced up by the piston when the latter reaches the top of the

cylinder; the oil then enters and displaces any air that may be lurking in the cavity.

It is a great improvement to the machine to supply the piston with a *relief-valve* opening upward; this may also be of metal, and contained within the body of the piston. Its use is to avoid the momentary condensation of the air in the receiver when the piston descends. The pump is worked by a lever in the manner represented in figure 16.

Fig. 16.



The air-pump may be used for condensing instead of for rarefying the air. If the cylinder (fig. 15) is filled with air from the opening (*i*), it may be forced by the rise of the piston through the valve (*a*) into a communicating chamber, and this operation may be frequently repeated.

To return to the atmosphere. Air possesses weight: a light flask or globe of glass, furnished with a stopcock and exhausted by the air-pump, weighs considerably less than when full of air. If the capacity of the vessel be equal to 100 cubic inches, this difference may amount to nearly 30 grains.

The mere fact of the pressure of the atmosphere may be demonstrated by securely tying a piece of bladder over the mouth of an open glass receiver, and then exhausting the air from beneath it; the bladder will become more and more concave, until it suddenly breaks. A thin square glass bottle, or a large air-tight tin box, may be crushed by withdrawing the support of the air in the inside. Steam-boilers have been often destroyed in this manner by collapse, in consequence of the accidental formation of a partial vacuum within.

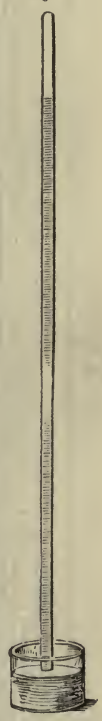
After what has been said on the subject of fluid pressure, it will scarcely be necessary to observe that the law of equality of pressure in all directions also holds good in the case of the atmosphere. The perfect mobility of the particles of air permits the transmission of the force generated by their gravity. The sides and bottom of an exhausted vessel are pressed upon with as much force as the top.

If a glass tube of considerable length could be perfectly exhausted of air, and then held in an upright position, with one of its ends dipping into a vessel of liquid, the latter, on being allowed access to the tube, would rise in its interior until the weight of the column balanced the pressure of the air upon the surface of the liquid. Now, if the density of this liquid were known, and the height and area of the column measured, means would be furnished for exactly estimating the amount of pressure exerted by the atmosphere. Such an instrument is the barometer: a straight glass tube is taken, about 36 inches in length, and sealed by the blowpipe flame at one extremity; it is then filled with clean,

dry mercury, care being taken to displace all air-bubbles, the open end stopped with a finger, and the tube inverted in the basin of mercury. On removing the finger, the fluid sinks away from the top of the tube, until it stands at the height of about 30 inches above the level of that in the basin. Here it remains supported by, and balancing the atmospheric pressure, the space above the mercury in the tube being of necessity empty.

The pressure of the atmosphere is thus seen to be capable of sustaining a column of mercury 30 inches in height, or thereabouts: now such a column, having an area of one inch, weighs between 14 and 15 pounds: consequently such must be the amount of the pressure exerted upon every square inch of the surface of the earth, and of the objects situated thereon, at least near the level of the sea. This enormous force is borne without inconvenience by the animal frame, by reason of its perfect uniformity in every direction; and it may be doubled, or even tripled, without injury.

Fig. 17.



A barometer may be constructed with other liquids besides mercury; but as the height of the column must always bear an inverse proportion to the density of the liquid, the length of tube required will be often considerable; in the case of water it will exceed 33 feet. It is seldom that any other liquid than mercury is employed in the construction of this instrument. The Royal Society of London possessed a water barometer at their apartments at Somerset House. Its construction was attended with great difficulties, and it was found impossible to keep it in repair.

It will now be necessary to consider a most important law which connects the volume occupied by a gas with the pressure made upon it, and is thus expressed:

The volume of gas is *inversely* as the pressure; the density and elastic force are *directly* as the pressure, and *inversely* as the volume.

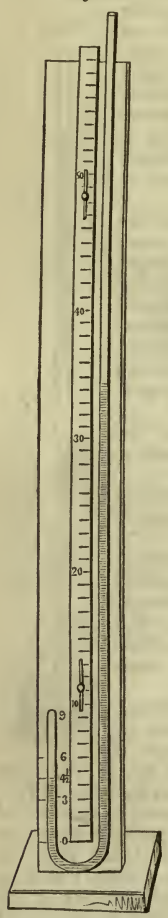
For instance, 100 cubic inches of gas under a pressure of 30 inches of mercury would expand to 200 cubic inches were the pressure reduced to one half, and shrink, on the contrary, to 50 cubic inches if the original pressure were doubled. The change of density must necessarily be in the inverse proportion to that of the volume, and the elastic force follows the same rule.

This, which is usually called the law of Mariotte, though really discovered by Boyle (1661), is easily demonstrable by direct experiment. A glass tube, about 7 feet in length, is closed at one end, and bent into the form represented in fig. 18, the open limb of the syphon being the longer. It is next attached to a board furnished with a movable scale of inches, and enough mercury is introduced to fill the bend, the level being evenly adjusted, and marked upon the board. Mercury is now poured into the tube until it is found that the inclosed air has been reduced to one half of its former volume; and on applying the scale, it will be found that the level of the mercury in the open part of the tube stands very nearly 30 inches above that in the closed portion. The pressure of an additional "atmosphere" has consequently reduced the bulk of the contained air to one half. If the experiment be still continued until the volume of air is reduced to a third, it will be found that the column measures 60 inches, and so in like proportion as far as the experiment is carried.

The above instrument is better adapted for illustration of the principle than for furnishing rigorous proof of the law; this has, however, been

done. MM. Arago and Dulong published, in the year 1830, an account of certain experiments made by them in Paris, in which the law in question had been verified to the extent of 27 atmospheres. And with rarefied air, of whatever degree of rarefaction, the law has been found true.

Fig. 18.



All gases are alike subject to this law, and all vapors of volatile liquids, when remote from their points of liquefaction.* It is a matter of the greatest importance in practical chemistry, since it gives the means of making corrections for pressure, or determining by calculation the change of volume which a gas would suffer by any given change of external pressure.

Let it be required, for example, to solve the following problem: We have 100 cubic inches of gas in a graduated jar, the barometer standing at 29 inches; how many cubic inches will it occupy when the column rises to 30 inches?—Now the volume must be inversely as the pressure: consequently a change of pressure in the proportion of 29 to 30 must be accompanied by a change of volume in the proportion of 30 to 29, the 30 cubic inches of gas contracting to 29 cubic inches under the conditions imagined. Hence the answer:

$$30 : 29 = 100 : 96{\cdot}67 \text{ cubic inches.}$$

The reverse of the operation will be obvious. The pupil will do well to familiarize himself with the simple calculations of correction for pressure.

From what has been said respecting the easy compressibility of gases, it will be at once seen that the atmosphere cannot have the same density, and cannot exert equal pressures at different elevations above the sea-level, but that, on the contrary, these must diminish with the altitude, and very rapidly. The lower strata of air have to bear the weight of those above them; they become, in consequence, denser and more compressed than the upper portions. The following table, which is taken from Prof. Graham's work, shows in a very simple manner the rule followed in this respect:

Height above the sea, in miles.	Volume of air.	Height of barometer, in inches.
0	1	30
2·705	2	15
5·41	4	7·5
8·115	8	3·75
10·82	16	1·875
13·525	32	0·9375
16·23	64	0·46875

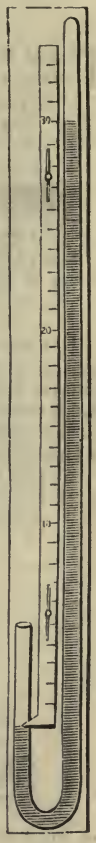
The numbers in the first column form an *arithmetical* series, by the constant addition of 2·705; those in the second column an increasing *geometrical* series, each being double its predecessor; and those in the third, a decreasing geometrical series, in which each number is the half of that standing above it.

* Near the liquefying point the law no longer holds; the volume diminishes *more rapidly* than the theory indicates, a smaller amount of pressure being then sufficient.

In ascending into the air in a balloon, these effects are well observed; the expansion of the gas within the machine, and the fall of the mercury in the barometer, soon indicate to the voyager the fact of his having left below him a considerable part of the whole atmosphere.

The invention of the barometer, which took place in the year 1643, by Torricelli, a pupil of the celebrated Galileo, speedily led to the observation that the atmospheric pressure at the same level is not constant, but possesses, on the contrary, a small range of variation, seldom exceeding in Europe 2 or 2·5 inches, and within the tropics usually confined within much narrower limits. Two kinds of variations are distinguished: regular or horary, and irregular or accidental. It has been observed that in Europe the height of the barometer is greatest at two periods in the twenty-four hours, depending upon the season. In winter, the first maximum takes place about 9 A. M., the first minimum at 3 P. M., after which the mercury again rises and attains its greatest elevation at 9 in the evening: in summer these hours of the aërial tides are somewhat altered. The accidental variations are much greater in amount, and render it extremely difficult to trace the regular changes above mentioned.

Fig. 19.



The barometer is applied with great advantage to the measurement of accessible heights, and it is also in daily use for foretelling the state of the weather; its indications are in this respect extremely deceptive, except in the case of sudden and violent storms, which are almost always preceded by a rapid fall in the mercurial column. It is often extremely useful in this respect at sea.

To the practical chemist a moderately good barometer is an indispensable article, since in all experiments in which volumes of gases are to be estimated, an account must be taken of the atmospheric pressure. Fig. 19 represents a very convenient and economical syphon-barometer for this purpose. A piece of new and stout tube, of about one third of an inch in diameter, is procured at the glass-house, sealed at one extremity, and bent into the syphon-form, as represented. Pure and warm mercury is next introduced by successive portions until the tube is completely filled, and the latter being held in an upright position, the level of the metal in the lower and open limb is conveniently adjusted by displacing a portion with a stick or glass rod. The barometer is, lastly, attached to a board, and furnished with a long scale, made to slide, which may be of box-wood, with a slip of ivory at each end. When an observation is to be taken, the lower extremity or zero of the scale is placed exactly even with the mercury in the short limb, and then the height of the column is at once read off.

HEAT.

IT will be convenient to consider the subject of heat under several sections, and in the following order:—

1. Expansion of bodies, or effects of variations of temperature in altering their dimensions.
2. Conduction, or transmission of heat.
3. Change of state.
4. Specific heat.
5. Sources of heat.
6. Dynamical theory of heat.

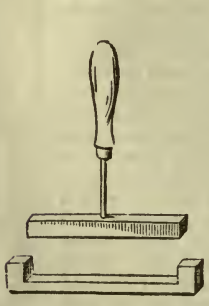
The phenomena of radiation must be deferred until a sketch has been given of the science of light.

EXPANSION.

If a bar of metal of such magnitude as to fit accurately to a gauge, when cold, be heated considerably, and again applied to the gauge, it will be found to have become enlarged in all its dimensions. When cold, it will once more enter the gauge.

Again, if a quantity of liquid contained in a glass bulb, furnished with a narrow neck, be plunged into hot water, or exposed to any other source

Fig. 20. *Fig.* 21. *Fig.* 22.



of heat, the liquid will mount in the stem, showing that its volume has been increased. The bulb, however, has likewise expanded by the heat, and its capacity has consequently been augmented. The rise of the liquid in the tube, therefore, denotes the difference between these two expansions.

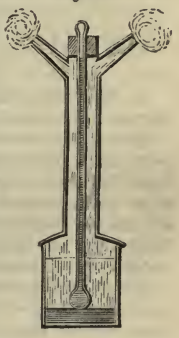
Or, if a portion of air be confined in any vessel, the application of a slight degree of heat will suffice to make it occupy a space sensibly larger.

This most general of all the effects of heat furnishes in the outset a principle, by the aid of which an instrument can be constructed capable of taking cognizance of changes of temperature in a manner equally accurate and convenient: such an instrument is the thermometer.

A capillary glass tube is chosen, of uniform diameter: one extremity is closed and expanded into a bulb, by the aid of the blowpipe flame, and the

other somewhat drawn out, and left open. The bulb is now cautiously heated by a spirit-lamp, and the open extremity plunged into a vessel of mercury, a portion of which rises into the bulb when the latter cools, replacing the air which had been expanded and driven out by the heat. By again applying the flame, and causing this mercury to boil, the remainder of the air is easily expelled, and the whole space filled with mercurial vapor. The open end of the tube must now be immediately plunged into the vessel filled with mercury; as the metallic vapors condense, the pressure of the external air forces the liquid metal into the instrument, until finally the tube is completely filled with mercury. The thermometer thus filled is now to be heated until so much mercury has been driven out by the expansion of the remainder, that its level in the tube shall stand at common temperatures at the point required. This being satisfactorily adjusted, the heat is once more applied, until the column rises quite to the top; and then the extremity of the tube is hermetically sealed by the blowpipe. The retraction of the mercury on cooling now leaves an empty space, which is essential to the perfection of the instrument.

Fig. 23.



The thermometer has yet to be graduated; and to make its indications comparable with those of other instruments, a scale, having at the least two fixed points, must be adapted to it.

It has been observed, that the temperature of melting ice, that is to say, of a mixture of ice and water, is always constant; a thermometer, already graduated, plunged into such a mixture, always marks the same degree of temperature, and a simple tube filled in the manner described and so treated, exhibits the same effect in the unchanged height of the little mercurial column, when tried from day to day. The freezing-point of water, or melting-point of ice, constitutes then one of the invariable temperatures demanded.

Another is to be found in the boiling-point of water, or, more accurately, in the temperature of steam which rises from boiling water. In order to give this temperature, which remains perfectly constant whilst the barometric pressure is constant, to the mercury of the thermometer, distilled water is made to boil in a glass vessel with a long neck, when the pressure is at 30 inches (fig. 23). The thermometer is then so placed that all the mercury is surrounded with steam. It quickly rises to a fixed point, and there it remains as long as the water boils, and the height of the barometer is unchanged.

The tube having been carefully marked with a file at these two points, it remains to divide the interval into degrees: this division is entirely arbitrary. The scale now most generally employed is the Centigrade, in which the space is divided into 100 parts, the zero being placed at the freezing-point of water. The scale is continued above and below these points, numbers below 0 being distinguished by the negative sign.

In England the division of Fahrenheit is still in use: the above-mentioned space is divided into 180 degrees; but the zero, instead of starting from the freezing-point of water, is placed 32 degrees below it, so that the temperature of ebullition is expressed by 212°.

The plan of Reaumur is nearly confined to a few places in the north of Germany and to Russia: in this scale the freezing-point of water is made 0°, and the boiling-point 80°.

It is unfortunate that a uniform system has not been generally adopted in graduating thermometers: this would render unnecessary the labor which now so frequently has to be performed of translating the language

of one scale into that of another. To effect this, presents, however, no great difficulty. Let it be required, for example, to know the degree of Fahrenheit's scale which corresponds to 60° C.

$$100° \text{ C} = 180° \text{ F, or } 5° \text{ C} = 9° \text{ F.}$$

Consequently,

$$5 : 9 = 60 : 108.$$

But then, as Fahrenheit's scale commences with 32° instead of 0°, that number must be added to the result, making 60° C = 140° F.

The rule then will be the following: — To convert Centigrade degrees into Fahrenheit degrees, multiply by 9, divide the product by 5, and add 32; to convert Fahrenheit degrees into Centigrade degrees, subtract 32, multiply by 5, and divide by 9.

The reduction of negative degrees, or those below zero of one scale into those of another scale, is effected in the same way. For example, to convert — 15° C. into degrees of Fahrenheit —

$$\text{We have} -15 \times \frac{9}{5} + 32 = -27 + 32 = +5 \text{ F.}$$

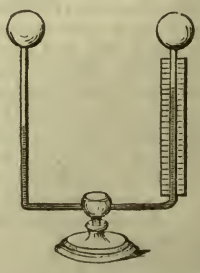
In this work, temperatures will always be given in Centigrade degrees, unless the contrary is expressly stated.

Mercury is usually chosen for making thermometers, on account of its regularity of expansion within certain limits, and because it is easy to have the scale of great extent, from the large interval between the freezing and boiling points of the metal. Other substances are sometimes used: alcohol is employed for estimating very low temperatures, because this liquid has not been frozen even at the lowest degree of cold which has been artificially produced.

Air-thermometers are also used for some few particular purposes; indeed, the first thermometer ever made was of this kind. There are two modifications of this instrument: in the first, the liquid into which the tube dips is open to the air; and in the second, shown in fig. 24, the atmosphere is completely excluded. The effects of expansion are in the one case complicated with those arising from changes of pressure, and in the other cease to be visible at all when the *whole* instrument is subjected to alterations of temperature, because the air in the upper and lower reservoir being equally affected by such changes, no alteration in the height of the fluid column

Fig. 24.

Fig. 25.



can occur. Accordingly, such instruments are called *differential* thermometers, since they serve to measure differences of temperature between the two portions of air, while changes affecting both alike are not indicated. Fig. 25 shows another form of the same instrument.

The air-thermometer may be employed for measuring all temperatures from the lowest to the highest; M. Pouillet has described one by which the heat of an air-furnace could be measured. The reservoir of this instrument is of platinum, and it is connected with a piece of apparatus by which the increase of volume experienced by the included air is determined.

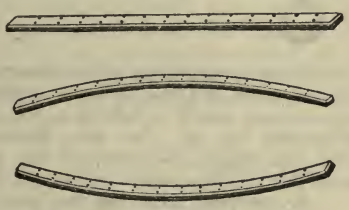
An excellent air-thermometer has been constructed and used by Rudberg, and more recently by Magnus and Regnault, for measuring the expansion of the air. Its construction depends on the law, that when air is heated and hindered from expanding, its tension increases in the same proportion in which it would have increased in volume if permitted to expand.

All bodies are enlarged in their dimensions by the application of heat, and reduced by its abstraction, or, in other words, contract on being artificially cooled: this effect takes place to a comparatively small extent with solids, to a larger amount in liquids, and most of all in the case of gases.

Each solid and liquid has a rate of expansion peculiar to itself; gases, on the contrary, expand nearly alike for the same increase of heat.

Expansion of Solids.—The difference of expansibility among solids is very easily illustrated by the following arrangement: a thin, straight bar of iron is firmly fixed, by numerous rivets, to a similar bar of brass: so long as the temperature at which the two metals were united remains unchanged, the compound bar preserves its straight figure; but any alteration of temperature gives rise to a corresponding curvature. Brass is more dilatable than iron; if the bar be heated, therefore, the former expands more than the latter, and forces the straight bar into a curve, whose convex side is the brass; if it be artificially cooled, the brass contracts more than the iron, and the reverse of this effect is produced.

Fig. 26.



This fact has received a most valuable application. It is not necessary to insist on the importance of possessing instruments for the accurate measurement of time; such are absolutely indispensable to the successful cultivation of astronomical science, and not less useful to the navigator, from the assistance they give him in finding the longitude at sea. For a long time, notwithstanding the perfection of finish and adjustment bestowed upon clocks and watches, an apparently insurmountable obstacle presented itself to their uniform and regular movement: this obstacle was the change of dimensions to which the regulating parts of the machine were subject by alterations of temperature. A clock may be defined as an instrument for registering the number of beats made by a pendulum: now the time of oscillation of a pendulum depends *principally* upon its length; any alteration in this condition will seriously affect the rate of the clock. The material of which the rod of the pendulum is composed is subject to expansion and contraction by changes of temperature; so that a pendulum

adjusted to vibrate seconds at 15·5° would go too slow if the temperature rose to 20°, from its becoming longer, and too fast if the temperature fell to 10°, from the opposite cause.

This great difficulty has been overcome by making the rod of a number of bars of iron and brass, or iron and zinc, metals whose rates of expansion are different, and arranging these bars in such a manner that the expansion in one direction of the iron shall be exactly compensated by that in the opposite direction of the brass or zinc, it is possible to maintain under all circumstances of temperature an invariable distance between the points of suspension and of oscillation. This is often called the *gridiron pendulum;* fig. 27 will clearly illustrate its principle; the shaded bars are supposed to be iron and the others zinc.

Fig. 27.

Fig. 28.

A still simpler compensation-pendulum is thus constructed. The weight or bob, instead of being made of a disc of metal, consists of a cylindrical glass jar containing mercury, which is held by a stirrup at the extremity of the steel pendulum-rod, fig. 28. The same increase of temperature which lengthens this rod, causes the volume of the mercury to enlarge, and its level to rise in the jar: the centre of gravity is thus elevated, and by properly adjusting the quantity of mercury in the glass, the virtual length of the pendulum may be made constant.

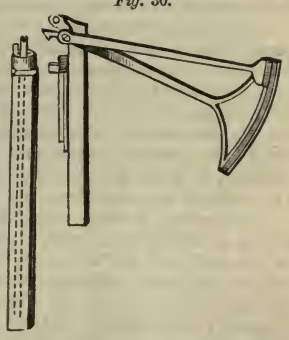
Fig. 29.

In watches, the governing power is a horizontal weighted wheel, set in motion in one direction by the machine itself, and in the other by a fine spiral spring. The rate of going depends greatly on the diameter of this wheel, and the diameter is of necessity subject to variation by change of temperature. To remedy the evil thus involved, the circumference of the balance-wheel is made of two metals having different rates of expansion, firmly soldered together, the more expansible being on the outside. The compound rim is also cut through in two places, as represented in the drawing. When the watch is exposed to a high temperature, and the diameter of the wheel becomes enlarged by expansion, each seg-

ment is made, by the same agency, to assume a sharper curve, whereby its centre of gravity is thrown inward, and the expansive effect completely compensated. Many other beautiful applications of the same principle might be pointed out: the metallic thermometer of M. Breguet is one of these.

Mr. Daniell very skilfully applied the expansion of a rod of metal to the measurement of temperatures above those capable of being indicated by the thermometer. A rod of iron or platinum, about five inches long, is dropped into a tube of black lead earthenware; a little cylinder of baked porcelain is put over it, and secured in its place by a platinum strap and a wedge of porcelain. When the whole is exposed to heat, the expansion of the bar drives forward the cylinder, which moves with a certain degree of friction, and shows, by the extent of its displacement, the lengthening which the bar has undergone. It remains, therefore, to measure the amount of its displacement, which must be very small, even when the heat has been exceedingly intense. This is effected by the contrivance shown in figure 30, in which the motion of the longer arm of the lever carrying the vernier of the scale is multiplied by 10, in consequence of its superior length. The scale itself is made comparable with that of the ordinary thermometer, by plunging the instrument into a bath of mercury near its point of congelation, and afterwards into another of the same metal in a boiling state, and marking off the interval. By this instrument the melting-point of cast iron was fixed at 1530° C. (2786° F.), and the greatest heat of a good wind-furnace at about 1815° C. (3390° F.)

Fig. 30.



The actual amount of expansion which different solids undergo by the same increase of heat has been carefully investigated. The following are some of the results of the best investigations, more particularly those of Lavoisier and Laplace. The fraction indicates the amount of expansion in length suffered by rods of the undermentioned bodies in passing from 0° to 100°:

Firwood*	$\frac{1}{245}$	Tempered steel	$\frac{1}{807}$
English flint glass	$\frac{1}{1248}$	Soft iron	$\frac{1}{819}$
Platinum†	$\frac{1}{1167}$	Gold	$\frac{1}{682}$
Common white glass‡	$\frac{1}{1160}$	Copper	$\frac{1}{584}$
Common white glass§	$\frac{1}{1147}$	Brass	$\frac{1}{535}$
Glass without lead	$\frac{1}{1142}$	Silver	$\frac{1}{524}$
Another specimen	$\frac{1}{1090}$	Lead	$\frac{1}{351}$
Steel untempered	$\frac{1}{527}$	Zinc	$\frac{1}{333}$

From the *linear* expansion, the *cubic* expansion (or increase of volume) may be calculated. When the expansion of a body in different directions is equal, as, for example, in glass, hammered metals, and generally in most uncrystallized substances, it will be sufficient to triple the fraction expressing the increase in one dimension. This rule does not hold true

* In the direction of the vessels — Kater.
† Borda.
‡ Dulong and Petit.
§ Lavoisier and Laplace; also Magnus.

for crystals belonging to irregular systems, for they expand unequally in the direction of the different axes.

Metals appear to expand pretty uniformly for equal increments of heat within the limits stated; but above the boiling-point of water the rate of expansion becomes irregular and more rapid.

The force exerted in the act of expansion is very great. In laying down railways, building iron bridges, erecting long ranges of steam-pipes, and in executing all works of the kind in which metal is largely used, it is indispensable to make provision for these changes of dimensions.

In consequence of glass and platinum having nearly the same amount of expansion, a thin platinum wire may be fused into a glass tube, without any fear that the glass will break on cooling.

A very useful little application of expansion by heat is that of the cutting of glass by a hot iron: this is constantly practised in the laboratory for a great variety of purposes. The glass to be cut is marked with ink in the required direction, and then a crack, commenced by any convenient method, at some distance from the desired line of fracture, may be led by the point of a heated iron rod along the latter with the greatest precision.

Expansion of Liquids.—The dilatation of a liquid may be determined by filling a thermometer with it, in which the relation between the capacity of the ball and that of the stem is exactly known, and observing the height of the column at different temperatures. It is necessary in this experiment to take into account the effects of the expansion of the glass itself, the observed result being evidently the *difference* of the two.

Liquids vary exceedingly in this particular. The following table is taken from Péclet's *Élements de Physique:*

Apparent Dilatation in Glass between 0° *and* 100°.

Water	$\frac{1}{22}$
Hydrochloric acid, sp. gr. 1·137	$\frac{1}{27}$
Nitric acid, sp. gr. 1·4	$\frac{1}{9}$
Sulphuric acid, sp. gr. 1·85	$\frac{1}{17}$
Ether	$\frac{1}{14}$
Olive oil	$\frac{1}{12}$
Alcohol	$\frac{1}{9}$
Mercury	$\frac{1}{64}$

Most of these numbers must be taken as representing mean results; for there are few liquids which, like mercury, expand regularly between these temperatures. Even mercury above 100° shows an unequal and increasing expansion, if the temperature indicated by the air-thermometer be used for comparison. This is shown by the following abstract of a table given by Regnault:

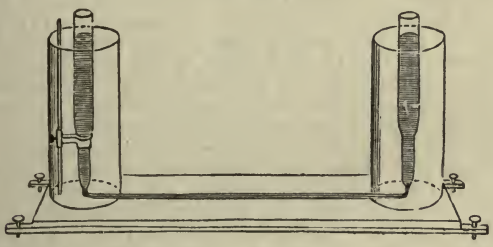
Reading of Air Thermometer.	Reading of Mercurial Thermometer.	Temperature deduced from the absolute expansion of Mercury.
0°	0°	0°
100°	100°	100°
200°	200°	202·78°
300°	301°	308·34°
350°	354°	362·16°

The absolute amount of expansion of mercury is, for many reasons, a point of great importance: it has been very carefully determined by a method independent of the expansion of the containing vessel. The apparatus employed for this purpose, first by MM. Dulong and Petit, and later by Regnault, is shown in fig. 31, divested, however, of many of its

subordinate parts. It consists of two upright glass tubes, connected at their bases by a horizontal tube of much smaller dimensions. Since a free communication exists between the two tubes, mercury poured into the one will rise to the same level in the other, provided its temperature is the same in both tubes; when this is not the case, the hotter column will be the taller, because the expansion of the metal diminishes its specific gravity, and the law of hydrostatic equilibrium requires that the height of such columns should be inversely as their densities. By the aid of the outer cylinders, one of the tubes is maintained constantly at 0°, while the other is raised, by means of heated water or oil, to any required temperature. The perpendicular heights of the columns may then be read off by a horizontal micrometer telescope, moving on a vertical divided scale.

These heights represent volumes of equal weight, because volumes of equal weight bear an inverse proportion to the densities of the liquids, so that the amount of expansion admits of being very easily calculated. Thus, let the column at 0° be six inches high, and that at 100°, 6·108 inches; the increase of height, 108 on 6000, or $\frac{1}{555}$ part of the actual cubical expansion.

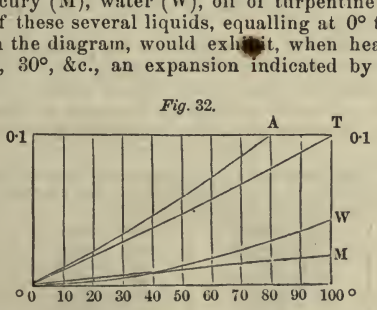
Fig. 31.



The indications of the mercurial thermometer are inaccurate when very high ranges of temperature are concerned, from the increased expansibility of the metal. The error thus caused is, however, nearly compensated for temperatures under 204·5° by the expansion of the glass tube. For higher temperatures a small correction is necessary, as the above table shows.

To what extent the expansion of different liquids may vary between the same temperatures is obvious from a glance at fig. 32, which represents the expansion of mercury (M), water (W), oil of turpentine (T), and alcohol (A). A column of these several liquids, equalling at 0° the tenfold height of the line 0 0·1 in the diagram, would exhibit, when heated to a temperature of 10°, 20°, 30°, &c., an expansion indicated by the distances at

Fig. 32.



which the perpendicular lines drawn over the numbers 10, 20, 30, &c., are intersected by the curves belonging to each of these liquids. Thus it is

seen that oil of turpentine, between 0° and 100°, expands very nearly $\frac{1}{10}$ of its volume, and that mercury, between the same limits of temperature, expands uniformly, while the rate of expansion of the other liquids increases with the rise of the temperature.

An exception to the regularity of expansion in liquids exists in the case of water; it is so remarkable, and its consequences so important, that it is necessary to advert to it particularly.

Let a large thermometer-tube be filled with water at the common temperature of the air, and then artificially cooled. The liquid will be observed to contract, until the temperature falls to about 4° C. (39·2° F., or 8°) above the freezing-point. After this a further reduction of temperature causes expansion instead of contraction in the volume of the water, and this expansion continues until the liquid arrives at its point of congelation, when so sudden and violent an enlargement takes place that the vessel is almost invariably broken. At the temperature of 4°, water is at its maximum density;* increase or diminution of heat produces upon it, for a short time, the same effect.

A beautiful experiment by Dr. Hope illustrates the same fact. If a tall jar filled with water at 10° or 15°, and having in it two small thermometers, one at the bottom and the other near the surface, be placed at rest in a very cold room, the following changes will be observed:—The thermometer at the bottom will fall more rapidly than that at the top, until it has attained the temperature of 4°, after which it will remain stationary. At length the upper thermometer will also mark 4°, but still continue to sink as rapidly as before, while that at the bottom remains stationary. It is easy to explain these effects: the water in the upper part of the jar is rapidly cooled by contact with the air; it becomes denser in consequence, and falls to the bottom, its place being supplied by the lighter and warmer liquid, which in its turn suffers the same change; and this circulation goes on until the whole mass of water has acquired its condition of maximum density, that is, until the temperature has fallen to 4°. Beyond this, loss of heat occasions expansion instead of contraction, so that the very cold water on the surface has no tendency to sink, but rather the reverse.

This singular anomaly in the behavior of water is attended with the most beneficial consequences in shielding the inhabitants of the waters from excessive cold. The deep lakes of the North American continent never freeze, the intense and prolonged cold of the winters of those regions being insufficient to reduce the temperature of such masses of water to 4°. Ice, however, of great thickness forms over the shallow portions and the rivers, and accumulates in mounds upon the beaches, where the waves are driven up by the winds

Above the freezing-point, sea-water has no point of maximum density. The more it is cooled the denser it becomes, until it solidifies at −2·6°.† The gradual expansion of pure water cooled below 4° must be carefully distinguished from the great and sudden increase of volume it exhibits in the act of freezing, in which respect it resembles many other bodies which

* According to the latest researches of Kopp, the point of greatest density of the water is 4·08° C. (39·34° F.). According to the determinations of this physicist, the volume of water = 1 at 0° C. changes when heated to the following volumes:

2° 0·99991	16° 1·00085	35° 1·00570	70° 1·02225
4° 0·99988	18° 1·00118	40° 1·00753	75° 1.02544
6° 0·99990	20° 1·00157	45° 1·00954	80° 1·02858
8° 0·99999	22° 1·00200	50° 1·01177	85° 1·03189
10° 1·00012	24° 1·00247	55° 1·01410	90° 1·03540
12° 1·00031	25° 1·00272	60° 0·01659	95° 1·03909
14° 1·00056	30° 1·00406	65° 1·01930	100° 1·04299

† Neumann, Poggendorff's Annalen, cxiii. 382.

expand on solidifying. The force thus exerted by freezing water is enormous. Thick iron shells quite filled with water, and exposed, with their fuse-holes securely plugged, to the cold of a Canadian winter night, have been found split on the following morning. The freezing of water in the joints and crevices of rocks is a most potent agent in their disintegration.

Expansion of Gases.—This is a point of great practical importance to the chemist, and happily we have very excellent evidence upon the subject. The following four propositions exhibit, at a single view, the principal facts of the case:

1. All gases expand nearly alike for equal increments of heat; and all vapors, when remote from their condensing points, follow the same law.
2. The rate of expansion is not altered by a change in the state of compression, or elastic force of the gas itself.
3. The rate of expansion is uniform for all degrees of heat.
4. The actual amount of expansion is equal to $\frac{1}{2\frac{1}{7}\frac{1}{3}}$ or $\frac{11}{3000}$ or 0·03666 of the volume of the gas at 0° Centigrade, for each degree of the same scale.*

It will be unnecessary to enter into any description of the methods of investigation by which these results have been obtained; the advanced student will find in Pouillet's *Éléments de Physique*, and in the papers of Magnus and Regnault,† all the information he may require.

In the practical manipulation of gases, it very often becomes necessary to make a correction for temperature, or to discover how much the volume of a gas would be increased or diminished by a particular change of temperature; this can be effected with great facility. Let it be required, for example, to find the volume which 100 cubic inches of any gas at 10° would become on the temperature rising to 20°.

The rate of expansion is $\frac{1}{2\frac{1}{7}\frac{1}{3}}$ or $\frac{11}{3000}$ of the volume at 0° for each degree; or 3000 measures at 0° become 3011 at 1°, 3022 at 2°, 3110 at 10°, and 3220 at 20°. Hence

Meas. at 10°.		Meas. at 20°.	=	Meas. at 10°.		Meas. at 20°.
3110	:	3220	=	100	:	103·537

If this calculation is required to be made on the Fahrenheit scale, it must be remembered that the zero of that scale is 32° below the melting-point of ice. Above this temperature the expansion for each degree of the Fahrenheit scale is $\frac{1}{4\frac{9}{2}}$ of the original volume.

This, and the correction for pressure, are operations of very frequent occurrence in chemical investigations, and the student will do well to become familiar with them.

Note.—Of the four propositions stated in the text, the first and second have recently been shown to be true within certain limits only; and the third, although in the highest degree probable, would be very difficult to demonstrate rigidly; in fact, the equal rate of expansion of air is assumed in all experiments on other substances, and becomes the standard by which the results are measured.

The rate of expansion for the different gases is *not* absolutely the same, but the difference is so small that for most purposes it may with perfect safety be neglected. Neither is the state of elasticity altogether indifferent,

* The fraction $\frac{11}{3000}$ is very convenient for calculation.

† Poggendorff's Annalen, iv. 1.—Ann. Chim. Phys., 3d series, iv. 5, and v. 52.—See also Watts's Dictionary of Chemistry, art. HEAT, vol. iii. p. 46.

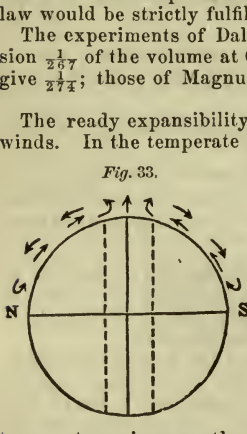
the expansion being sensibly *greater* for an equal rise of temperature when the gas is in a compressed state.

It is important to notice that the greatest deviations from the rule are exhibited by those gases which, as will hereafter be seen, are most easily liquefied, such as carbon dioxide, cyanogen, and sulphur dioxide; and that the discrepancies become smaller and smaller as the elastic force is lessened; so that, if means existed for comparing the different gases in states *equally distant* from their points of condensation, there is reason to believe that the law would be strictly fulfilled.

The experiments of Dalton and Gay-Lussac give for the rate of expansion $\frac{1}{267}$ of the volume at 0°: this is no doubt too high. Those of Rudberg give $\frac{1}{274}$; those of Magnus and of Regnault $\frac{1}{273}$.

The ready expansibility of air by heat gives rise to the phenomena of winds. In the temperate regions of the earth these are very variable and uncertain, but within and near the tropics a much greater regularity prevails; of this the *trade-winds* furnish a beautiful example.

Fig. 33.



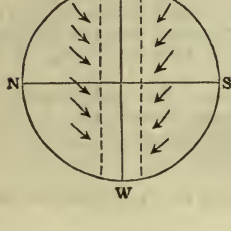
The smaller degree of obliquity with which the sun's rays fall in the localities mentioned, occasions the broad belt thus stretching round the earth to become more heated than any other part of the surface. The heat thus acquired by absorption is imparted to the lower stratum of air, which, becoming expanded, rises, and gives place to another; and in this manner an ascending current is established, the colder and heavier air streaming in laterally from the more temperate regions, north and south, to supply the partial vacuum thus occasioned. A circulation so commenced will be completed, in obedience to the laws of hydrostatics, by the establishment of counter-currents in the higher parts of the atmosphere, having directions the reverse of those on the surface.

Such is the effect produced by the unequal heating of the equatorial parts; or, more correctly, such would be the effect were it not greatly modified by the earth's movement of rotation.

As the circumference of the earth is, in round numbers, about 24,000 miles, and since it rotates on its axis, from west to east, once in 24 hours, the equatorial parts must have a motion of 1000 miles per hour; this velocity diminishes rapidly toward each pole, where it is reduced to nothing.

The earth in its rotation carries with it the atmosphere, whose velocity of movement corresponds, in the absence of disturbing causes, with that part of the surface immediately below it. The air which rushes toward the equator to supply the place of that raised aloft by its diminished density, brings with it the degree of momentum belonging to that portion of the earth's surface from which it set out, and as this momentum is less than that of the earth under its new position, the earth itself travels faster than the air immediately over it, thus producing the effect of a wind blowing in a contrary direction to that of its own motion. The original north and south winds are thus deviated from their primitive directions, and made to blow more or less from the eastward, so that

Fig. 34.



the combined effects of the unequal heating and of the movement of rotation is to generate in the northern hemisphere a constant north-east wind, and in the southern hemisphere an equally constant south-east wind.

In the same manner the upper or return current is subject to a change of direction in the reverse order; the rapidly moving wind of the tropics, transferred laterally towards the poles, is soon found to travel faster than the earth beneath it, producing the effect of a westerly wind, which modifies the primary current.

The regularity of the trade-winds is much interfered with by the neighborhood of large continents, which produce local effects upon a scale sufficiently great to modify deeply the direction and force of the wind. This is the case in the Indian Ocean. They usually extend from about the 28th degree of latitude in both hemispheres to within 8° of the equator, but are subject to some variations in this respect. Between them, and also beyond their boundaries, lie belts of calms and light variable winds; and beyond these latter, extending into higher latitudes in both hemispheres, westerly winds usually prevail. The general direction of the trade-wind of the Northern hemisphere is E.N.E., and that of the Southern hemisphere E.S.E.

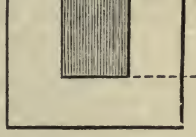
The trade-winds, it may be remarked, furnish an admirable physical proof of the reality of the earth's movement of rotation.

The theory of the action of chimneys, and of natural and artificial ventilation, belongs to the same subject.

Let the reader turn to the demonstration given of the Archimedean hydrostatic theorem: let him once more imagine a body immersed in water, and having a density equal to that of the water; it will remain in equilibrium in any part beneath the surface, and for these reasons: The force which presses it downward is the weight of the body added to the weight of the column of water above it; the force which presses it upward is the weight of a column of water equal to the height of both conjoined; — the density of the body is that of water, that is, it weighs as much as an equal bulk of that liquid; consequently, the downward and upward forces are equally balanced, and the body remains at rest.

Next, let the circumstances be altered; let the body be lighter than an equal bulk of water; the pressure upward of the column of water *a c* is no longer compensated by the downward pressure of the corresponding column of solid and water above it; the former force preponderates, and the body is driven upward. If, on the contrary, the body be specifically heavier than water, then the latter force has the ascendency, and the body sinks.

Fig. 35.



All things so described exist in a common chimney; the solid body, of the same density as that of the fluid in which it floats, is represented by the air in the chimney funnel; the space *a b* represents the whole atmosphere above it. When the air inside and outside the chimney is at the same temperature, equilibrium takes place, because the downward tendency of the air within is counteracted by the upward pressure of that without.

Now, let the chimney be heated; the air suffers expansion, and a portion is expelled; the chimney therefore contains a smaller weight of air than it did before; the external and internal columns no longer balance each other, and the warmer and lighter air is forced upward from below, and its place supplied by cold air. If the brick-work, or other material of which the chimney is constructed, retain its temperature, this second por-

tion of air is disposed of like the first, and the ascending current continues, so long as the sides of the chimney are hotter than the surrounding air.

Sometimes, owing to sudden changes of temperature in the atmosphere, the chimney may happen to be colder than the air about it. The column within forthwith suffers contraction of volume; the deficiency is filled up from without, and the column becomes heavier than one of similar height on the outside; the result is, that it falls out of the chimney, just as the heavy body sinks in the water, and has its place occupied by air from above. A descending current is thus produced, which may be often noticed in the summer season, by the smoke from neighboring chimneys finding its way into rooms which have been for a considerable time without fire.

The ventilation of mines has long been conducted upon the same principle, and more recently it has been applied to dwelling-houses and assembly-rooms. The mine is furnished with two shafts, or with one shaft divided throughout by a diaphragm of boards; and these are so arranged, that air forced down the one shall traverse the whole extent of the workings before it escapes by the other. A fire kept up in one of these shafts, by rarefying the air within, and causing an ascending current, occasions fresh air to traverse every part of the mine, and sweep before it the noxious gases but too frequently present.

CONDUCTION OF HEAT.

Different bodies possess very different conducting powers with respect to heat: if two similar rods, the one of iron, the other of glass, be held in the flame of a spirit-lamp, the iron will soon become too hot to be touched, while the glass may be grasped with impunity within an inch of the red-hot portion.

Experiments made by analogous but more accurate methods have established a numerical comparison of the conducting powers of many bodies. The following may he taken as a specimen: —

Silver	1000	Steel	116
Copper	736	Lead	85
Gold	532	Platinum	84
Brass	236	German silver	63
Tin	145	Bismuth	18
Iron	119		

As a class, the metals are by very far the best conductors, although much difference exists between them; stones, dense woods, and charcoal follow next in order: then liquids in general, and gases, whose conducting power is almost inappreciable.

Under favorable circumstances, nevertheless, both liquids and gases may become rapidly heated: heat applied to the bottom of the containing vessel is very speedily communicated to its contents: this, however, is not so much by conduction as by convection, or carrying. A complete circulation is set up; the portions in contact with the bottom of the vessel get heated, become lighter, and rise to the surface, and in this way the heat becomes communicated to the whole. If these movements be prevented by dividing the vessel into a great number of compartments, the really low conducting power of the substance is made evident; and this is the reason why certain organic fabrics, as wool, silk, feathers, and porous bodies in general, the cavities of which are full of air, exhibit such feeble powers of conduction.

The circulation of heated water through pipes is now extensively applied to the warming of buildings and conservatories; and in chemical works a serpentine metal tube containing hot oil is often used for heating stills and evaporating-pans: the two extremities of the tube are connected with the

ends of another spiral built into a small furnace at the lower level, and an unintermitting circulation of the liquid takes place as long as heat is applied.

CHANGE OF STATE.

Solid bodies when heated are expanded; many are liquefied, *i. e.*, they fuse. The fusion of solids is frequently preceded by a gradual softening, more especially when the temperature approaches the point of fusion. This phenomenon is observed in the case of wax or iron. In the case of other solids — of zinc and lead, for instance — and several other metals, this softening is not observed. Generally, bodies expand during the process of fusion; an exception to this rule is water, which expands during freezing (10 vol. of water produce nearly 11 vol. of ice), while ice when fusing produces a proportionately smaller volume of water. The expansion of bodies during fusion, and at temperatures preceding fusion, or the contraction during solidification and further refrigeration, is very unequal. Wax expands considerably before fusing, and comparatively little during fusion itself. Wax, when poured into moulds, fills them perfectly during solidification, but afterwards contracts considerably. Stearic acid, on the contrary, expands very little before fusion, but rather considerably during fusion, and consequently pure stearic acid when poured into moulds solidifies to a rough porous mass, contracting little by further cooling. The addition of a little wax to stearic acid prevents the powerful contraction in the moment of solidification, and renders it more fit for being moulded.

Latent Heat of Fusion. — During fusion bodies absorb a certain quantity of heat, which is not indicated by the thermometer; at a given temperature — the fusing-point, for instance — a certain weight of substance contains when solid less heat than when liquid.

If equal weights of water at 0° and water at 79° be mixed, the temperature of the mixture will be the mean of the two temperatures, or 39·5°. If the same experiment be repeated with snow or finely-powdered ice at 0°, and water at 79°, the temperature of the whole will be only 0°, *but the ice will have been melted.*

$$\left.\begin{array}{l}1 \text{ lb. of water at } 0^\circ \\ 1 \text{ lb. of water at } 79^\circ\end{array}\right\} = 2 \text{ lb. water at } 39{\cdot}5^\circ$$

$$\left.\begin{array}{l}1 \text{ lb. of ice at } 0^\circ \\ 1 \text{ lb. of water at } 79^\circ\end{array}\right\} = 2 \text{ lb. water at } 0^\circ$$

In the last experiment, therefore, as much heat has been apparently lost as would have raised a quantity of water equal to that of the ice through a range of 79°.

The heat, thus become insensible to the thermometer in effecting the liquefaction of the ice, is called *latent heat*, or, better, *heat of fluidity*.

Again, let a perfectly uniform source of heat be imagined, of such intensity that a pound of water placed over it would have its temperature raised 5° per minute. Starting with water at 0°, in rather less than 16 minutes its temperature would have risen 79°; but the same quantity of ice at 0°, exposed for the same interval of time, would not have its temperature raised a single degree. But, then, it would have become water; the heat received would have been exclusively employed in effecting the change of state.

This heat is not lost, for when the water freezes it is again evolved. If a tall jar of water, covered to exclude dust, be placed in a situation where it shall be quite undisturbed, and at the same time exposed to great cold, the temperature of the water may be reduced 10° or more below its freez-

ing-point without the formation of ice; * but then, if a little agitation be communicated to the jar, or a grain of sand dropped into the water, a portion instantly solidifies, and the temperature of the whole rises to 0°; the heat disengaged by the freezing of a small portion of the water will have been sufficient to raise the whole contents of the jar 5°.

This curious condition of instable equilibrium shown by the very cold water in the preceding experiment, may be reproduced with a variety of solutions which tend to crystallize or solidify, but in which that change is for a while suspended. Thus, a solution of crystallized sodium sulphate in its own weight of warm water, left to cool in an open vessel, deposits a large quantity of the salt in crystals. If the warm solution, however, be filtered into a clean flask, which when full is securely corked and set aside to cool undisturbed, no crystals will be deposited, even after many days, until the cork is withdrawn and the contents of the flask violently shaken. Crystallization then rapidly takes place in a very beautiful manner, and the whole becomes perceptibly warm.

The law thus illustrated in the case of water is perfectly general. Whenever a solid becomes a liquid, a certain fixed and definite amount of heat disappears, or becomes latent; and conversely, whenever a liquid becomes a solid, heat to a corresponding extent is given out.

The following table exhibits the melting points of several substances, and their latent heats of fusion expressed in gram-degrees — that is to say, the numbers in the column headed "latent heat" denote the number of grams of water the temperature of which would be raised 1° Centigrade by the quantity of heat required to fuse one grain of the several solids: —

Substance.	Melting Point.	Latent Heat.	Substance.	Melting Point.	Latent Heat.
Mercury . .	—39°	2·82	Tin	235°	14·25
Phosphorus	44	5·0	Silver	1000	21·1
Lead . . .	332	5·4	Zinc	433	28·1
Sulphur . .	115	9·4	Calcium chloride $(CaCl_2\ 6H^2O)$.	28·5	40·7
Iodine . .	107	11·7			
Bismuth . .	270	12·6	Potassium nitrate . .	339	47·4
Cadmium .	320	13·6	Sodium nitrate . .	310·5	63·0

When a solid substance can be made to liquefy by a weak chemical attraction, cold results, from sensible heat becoming latent. This is the principle of the many frigorific mixtures to be found described in some of the older chemical treatises. When snow or powdered ice is mixed with common salt, and a thermometer plunged into the mass, the mercury sinks to —17·7°C. (0° F.), while the whole after a short time becomes fluid by the attraction between the water and the salt; such a mixture is very often used in chemical experiments to cool receivers and condense the vapors of volatile liquids. Powdered crystallized calcium chloride and snow produce cold enough to freeze mercury. Even powdered potassium nitrate,

* Fused bodies, when cooled down to or below their fusing point, frequently remain liquid, more especially when not in contact with solid bodies. Thus, water in a mixture of oil of almonds and chloroform, of specific gravity equal to its own, remains liquid to —10°: in a similar manner fused sulphur or phosphorus, floating in a solution of zinc chloride of appropriate concentration, retains the liquid condition at temperatures 40° below its fusing point. Liquid bodies, thus cooled below their fusing point, frequently solidify when touched with a solid substance, invariably when brought in contact with a fragment of the same body in the solid condition.

or sal-ammoniac, or ammonium nitrate, dissolved in water, occasions a very notable depression of temperature: in every case, in short, in which solution is unaccompanied by energetic chemical action, cold is produced.

No relation can be traced between the actual melting-point of a substance, and its latent heat when in the fused state.

Latent Heat of Vaporization. — A law of exactly the same kind as that described affects universally the gaseous condition; change of state from solid or liquid to gas is accompanied by absorption of sensible heat, and the reverse by its disengagement. The latent heat of steam and other vapors may be ascertained by a mode of investigation similar to that employed in the case of water.

When water at 0° is mixed with an equal weight of water at 100°, the whole is found to possess the mean of the two temperatures, or 50°; on the other hand, 1 part by weight of *steam* at 100°, when condensed in cold water, is found to be capable of raising 5·4 parts of the latter from the freezing to the boiling-point, or through a range of 100°. Now $100 \times 5{\cdot}4 = 540°$; that is to say, steam at 100°, in becoming water at 100°, parts with enough heat to raise a weight of water equal to its own (if it were possible) 540°, of the thermometer. When water passes into steam, the same quantity of sensible heat becomes latent.

The vapors of other liquids seem to have less latent heat than that of water. The following table is by Dr. Th. Andrews, and serves well to illustrate this point. The latent heats are expressed, as in the last table, in gram-degrees:

Vapor of water	535·90°
" alcohol	202·40
" ether	90·45
" oxalic ether	72·72
" acetic ether	92·68
" ethylic iodide	46·87
" pyroxylic spirit	263·70
" carbon bisulphide	86·67
" tin tetrachloride	30·35
" bromine	45·66
" oil of turpentine	74·03

Ebullition is occasioned by the formation of bubbles of vapor within the body of the evaporating liquid, which rise to the surface like bubbles of permanent gas. This occurs in different liquids at very different temperatures. Under the same circumstances, the boiling-point is quite constant, and often becomes a physical character of great importance in distinguishing liquids which much resemble each other. A few cases may be cited in illustration:

Substance.	Boiling-point.
Aldehyde	20·8°
Ether	34·9
Carbon bisulphide	46·1
Alcohol	78·4
Water	100
Nitric acid, strong	120
Oil of turpentine	157
Sulphuric acid	326·6
Mercury	350

For ebullition to take place, it is necessary that the elasticity of the vapor should be able to overcome the cohesion of the liquid and the pres-

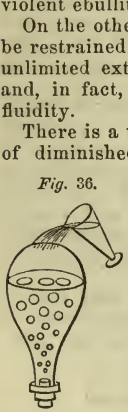
sure upon its surface: hence the extent to which the boiling-point may be modified.

Water, under the usual pressure of the atmosphere, boils at 100° (212° F.): in a partially exhausted receiver or on a mountain-top it boils at a much lower temperature: and in the best vacuum of an excellent air-pump, over oil of vitriol, which absorbs the vapor, it will often enter into violent ebullition while ice is in the act of forming upon the surface.

On the other hand, water confined in a very strong metallic vessel may be restrained from boiling by the pressure of its own vapor to an almost unlimited extent; a temperature of 177° or 204° is very easily obtained; and, in fact, it is said that it may be made red-hot, and yet retain its fluidity.

There is a very simple and beautiful experiment illustrative of the effect of diminished pressure in depressing the boiling-point of a liquid. A little water is made to boil for a few minutes in a flask or retort placed over a lamp, until the air has been chased out, and the steam issues freely from the neck. A tightly fitting cork is then inserted, and the lamp at the same moment withdrawn. When the ebullition ceases, it may be renewed at pleasure for a considerable time by the affusion of cold water, which, by condensing the vapor within, occasions a partial vacuum.

Fig. 36.



The nature of the vessel, or, rather, the state of its surface, exercises an influence upon the boiling-point, and this to a much greater extent than was formerly supposed. It has long been noticed that in a metallic vessel water boils, under the same circumstances of pressure, at a temperature one or two degrees below that at which ebullition takes place in glass; but it has lately been shown * that by particular management a much greater difference can be observed. If two similar glass flasks be taken, the one coated in the inside with a film of shellac, and the other completely cleansed by hot sulphuric acid, water heated over a lamp in the first will boil at 99·4°, while in the second it will often rise to 105° or even higher; a momentary burst of vapor then ensues, and the thermometer sinks a few degrees, after which it rises again. In this state, the introduction of a few metallic filings, or angular fragments of any kind, occasions a lively disengagement of vapor, while the temperature sinks to 100°, and there remains stationary. These remarkable effects must be attributed to an attraction between the surface of the vessel and the liquid.

When out of contact with solid bodies, liquids not only solidify with reluctance, but also assume the gaseous condition with greater difficulty. Drops of water or of aqueous saline solutions floating on the contact-surface of two liquids, of which one is heavier and the other lighter, may be heated from 10 to 20 degrees above the ordinary boiling-point; explosive ebullition, however, is instantaneously induced by contact with a solid substance.

A cubic inch of water in becoming steam under the ordinary pressure of the atmosphere expands into 1696 cubic inches, or nearly a cubic foot.

Steam, *not in contact with water*, is affected by heat in the same manner as the permanent gases; its rate of expansion and increase of elastic force are practically the same. When water is present, the rise of temperature increases the quantity and density of the steam, and hence the elastic force increases in a far more rapid proportion.

This elastic force of steam in contact with water, at different tempera-

* Marcet 'Ann. Chim. Phys.' 3d series, v. 449.

tures, has been very carefully determined by Arago and Dulong, and lately by Magnus and Regnault. The force is expressed in atmospheres: the absolute pressure upon any given surface can be easily calculated, allowing 14·6 lb per square inch to each atmosphere. The experiments were carried to twenty-five atmospheres; at which point the difficulties and danger became so great as to put a stop to the inquiry: the rest of the table is the result of calculations founded on the data so obtained:

Pressure of Steam in atmospheres.	Corresponding temperature.	Pressure of Steam in atmospheres.	Corresponding temperature.
1	100°	3	135°
1·5	112	3·5	140·5
2	122	4	145·5
2·5	129	4·5	149
5	153	17	207
5·5	157	18	209
6	160	19	212
6·5	163	20	214
7	167	21	217
7·5	169	22	219
8	172	23	222
9	177	24	224
10	182	25	226
11	186	30	236
12	190	35	245
13	194	40	253
14	197	45	255
15	200·5	50	266
16	203		

It is very interesting to know the amount of heat requisite to convert water of any given temperature into steam of the same or another given temperature. The most exact experiments on this subject have been made by Regnault. He arrived at this result, that when the unit-weight of steam at the temperature $t°$ is converted into water of the same temperature, and then cooled to 0°, it gives out the quantity of heat T, which is represented by the formula:

$$T = 606 \cdot 5 + 0 \cdot 305\, t.$$

This formula appears to hold good for temperatures above and below the ordinary boiling-point of water. The following table gives the values of T, corresponding to the respective temperatures in the first columns:

t	T
0°	606·5°
50	621·7
100	637·0
150	652·2
200	667·5

T is called the total heat of steam, being the heat required to raise water from 0° to t, together with that which becomes latent by the transformation of water of t into steam at t. Regnault states, as a result of some very delicate experiments, that the heat necessary to raise a unit-weight of water from 0° to t is not exactly denoted by t; the discrepancy, however, is so small that it may be disregarded. Employing the approximate value, the

latent heat of steam, L, at any temperature will be found by subtracting t from the total heat; or, according to the formula:

$$L = 606{\cdot}5 - 0{\cdot}595\ t.$$

This equation shows us the remarkable fact that the latent heat of steam diminishes as the temperature rises. Before Regnault's experiments were made, two laws of great simplicity were generally admitted, one of which, however, contradicted the other. Watt concluded, from experiments of his own, as well as from theoretical speculations, that the total heat of steam would be the same at all temperatures. Were this true, equal weights of steam passed into cold water would always exhibit the same heating power, no matter what the temperature of the steam might be. Exactly the same *absolute* amount of heat, and consequently the same quantity of fuel, would be required to evaporate a given weight of water *in vacuo* at a temperature which the hand can bear, or under great pressure, and at a high temperature. Watt's Law, though agreeing well with the rough practical results obtained by engineers, is only approximately true; and the same may be said of the deductions which have just been made from it. The second law, in opposition to Watt's, is that of Southern, stating the latent heat of steam to be the same at all temperatures. Regnault's researches have shown that neither Watt's law (T constant), nor Southern's law (L constant) is correct.

The economical applications of steam are numerous and extremely valuable: they may be divided into two classes: those in which the heating power is employed, and those in which its elastic force is brought into use.

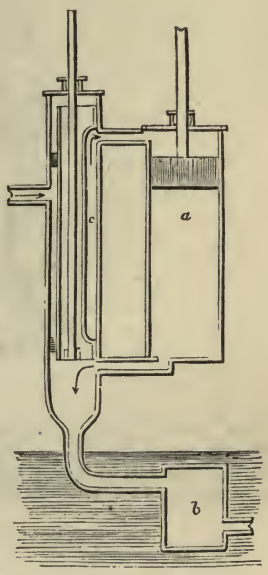
The value of steam as a source of heat depends upon the facility with which it may be conveyed to distant points, and upon the large amount of latent heat it contains, which is disengaged in the act of condensation. An invariable temperature of 100°, or higher, may be kept up in the pipes or other vessels in which the steam is contained by the expenditure of a very small quantity of the latter. Steam-baths of various forms are used in the arts with great convenience, and also by the scientific chemist for drying filters and other objects where excessive heat would be hurtful: a very good instrument of the kind was contrived by Mr. Everitt. It is merely a small kettle (fig. 37), surmounted by a double box or jacket, into which the substance to be dried is put, and loosely covered by a card. The apparatus is placed over a lamp, and may be left without attention for many hours. A little hole in the side of the jacket gives vent to the excess of steam.

The principle of the steam-engine may be described in a few words: its mechanical details do not belong to the design of the present volume. The machine consists essentially of a cylinder or metal *a* (fig. 38), in which a closely fitting solid piston works, the rod of which passes, air-tight, through a stuffing-box at the top of the cylinder, and is connected with the machinery to be put in motion, directly, or by the intervention of an oscillating beam. A pipe communicates with the interior of the cylinder, and also with a vessel surrounded with cold water, called the condenser *b*, into which a jet of cold water can at pleasure be introduced. A sliding-valve arrangement, shown at *c*, serves to open a communication between the boiler and the cylinder, and between the cylinder and the condenser in such a manner that while the steam is allowed to press with all its force upon one side of the piston, the other, open to the condenser, is necessarily vacuous. The valve is shifted by the

Fig. 37.

engine itself at the proper moment, so that the piston is alternately driven by the steam up and down against a vacuum. A large air-pump, not shown in the engraving, is connected with the condenser, and serves to remove any air that may enter the cylinder, and also the water produced by condensation, together with that which may have been injected.

Fig. 38.



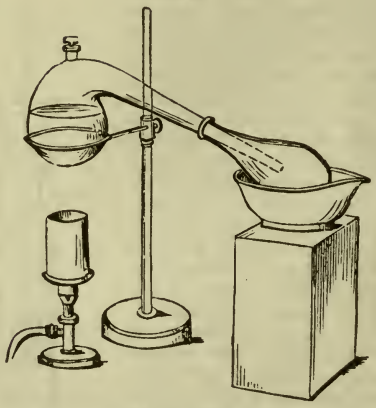
Such is the vacuum or condensing steam-engine. In what is called the high-pressure engine, the condenser and air-pump are suppressed, and the steam is allowed to escape at once from the cylinder into the atmosphere. It is obvious that in this arrangement the steam has to overcome the whole pressure of the air, and a much greater elastic force is required to produce the same effect; but this is to a very great extent compensated by the absence of the air-pump and the increased simplicity of the whole machine. Large engines, both on shore and in steamships, are usually constructed on the condensing principle, the pressure seldom exceeding six or seven pounds per square inch above that of the atmosphere; for small engines the high-pressure plan is, perhaps, preferable. Locomotive engines are of this kind.

A peculiar modification of the steam-engine, employed in Cornwall, for draining the deep mines of that country, is now getting into use elsewhere for other purposes. In this machine, economy of fuel is carried to a most extraordinary extent, engines having been known to perform the *duty* of raising more than 100,000,000 lbs. of water one foot high by the consumption of a single bushel of coals. The engines are single-acting, the down-stroke, which is made against a vacuum, being the effective one, and employed to lift the enormous weight of the pump-rods in the shaft of the mine. When the piston reaches the bottom, the communication both with the boiler and the condenser is cut off, while an *equilibrium-valve* is opened connecting the upper and lower extremities of the cylinder, whereupon the weight of the pump-rods draws the piston to the top and makes the up-stroke. The engine is worked *expansively*, as it is termed, steam of high tension being employed, which is cut off at one-eighth or even one-tenth of the stroke.

The process of distillation, which may now be noticed, is very simple: its object is either to separate substances which rise in vapor at different temperatures, or to part a volatile liquid from a substance incapable of volatilization. The same process applied to bodies which pass directly from the solid to the gaseous condition, and the reverse, is called *sublimation.* Every distillatory apparatus consists essentially of a boiler, in which the vapor is raised, and of a condenser, in which it returns to the liquid or solid condition. In the still employed for manufacturing purposes, the latter is usually a spiral metal tube immersed in a tub of water. The common retort and receiver constitute the simplest arrangement for distillation on the small scale; the retort is heated by a gas lamp, and the receiver is kept cool, if necessary, by a wet cloth, or it may be surrounded with ice. (Fig. 39.)

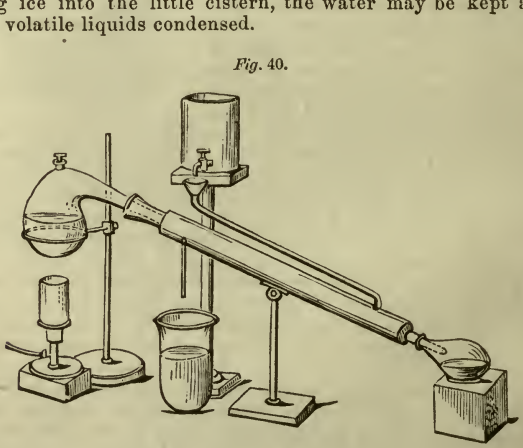
Liebig's condenser * (fig. 40) is a very valuable instrument in the laboratory; it consists of a glass tube tapering from end to end, fixed by per-

Fig. 39.



forated corks in the centre of the metal pipe, provided with tubes so arranged that a current of cold water may circulate through the apparatus. By putting ice into the little cistern, the water may be kept at 0°, and extremely volatile liquids condensed.

Fig. 40.



Liquids evaporate at temperatures below their boiling-points: in this case the evaporation takes place slowly from the surface. Water, or alcohol, exposed in an open vessel, at the temperature of the air, gradually disappears; the more rapidly, the warmer and drier the air.

This fact was formerly explained by supposing that air and gases in general had the power of dissolving and holding in solution certain quan-

[*Invented by Weitzel, the elder, of Stockholm, and well described and figured in Gray's Operative Chemist.—R. B.]

tities of liquids, and that this power increased with the temperature: such an idea is incorrect.

If a barometer-tube be carefully filled with mercury and inverted in the usual manner, and then a few drops of water passed up the tube into the vacuum above, a very remarkable effect will be observed; — the mercury will be depressed to a small extent, and this depression will increase with increase of temperature. Now, as the space above the mercury is void of air, and the weight of the few drops of water quite inadequate to account for this depression, it must of necessity be imputed to the vapor which instantaneously rises from the water into the vacuum; and that this effect is really due to the elasticity of the aqueous vapor, is easily proved by exposing the barometer to a heat of 100° C. (212° F.), when the depression of the mercury will be complete, and it will stand at the same level within and without the tube; indicating that at that temperature the elasticity of the vapor is equal to that of the atmosphere — a fact which the phenomenon of ebullition has already shown.

Fig. 41.

By placing over the barometer a wide open tube dipping into the mercury below, and then filling this tube with water at different temperatures, the tension of the aqueous vapor for each degree of the thermometer may be accurately determined by its depressing effect upon the mercurial column; the same power which forces the latter *down* one inch against the pressure of the atmosphere, would of course *elevate* a column of mercury to the same height against the vacuum, and in this way the tension may be conveniently expressed. The following table was drawn up by Dalton, to whom we owe the method of investigation:

Temperature. F.	C.	Tension in inches of mercury.	Temperature. F.	C.	Tension in inches of mercury.
32°	0°	0·200	130°	54·4°	4·34
40	4·4	0·263	140	60	5·74
50	10	0·375	150	65·5	7·42
60	15·5	0·524	160	71·1	9·46
70	21·1	0 721	170	76·6	12·13
80	26·6	1·000	180	82·2	15·15
90	32·2	1·360	190	87·7	19·00
100	37·7	1·860	200	93·3	23·64
110	43·3	2·530	212	100	30 00
120	48·8	3·330			

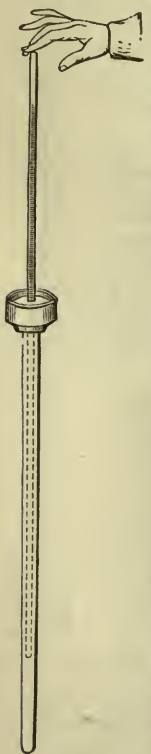
Another table representing the tension of the vapor of water, drawn up by Regnault, is given at the end of the work.

Other liquids tried in this manner are found to emit vapors of greater or less tension, for the same temperature, according to their different degrees of volatility: thus, a little ether introduced into the tube depresses the mercury 10 inches or more at the ordinary temperature of the air; oil of vitriol, on the other hand, does not emit any sensible quantity of vapor until a much greater heat is applied; and that given off by mercury itself in warm summer weather, although it may be detected by very delicate means, is far too little to exercise any effect upon the barometer. In the case of water, the evaporation is quite distinct and perceptible at the lowest temperatures, when frozen to solid ice in the barometer-tube: snow on the ground, or on a house-top, may often be noticed to vanish, from the same cause, day by day in the depth of winter, when melting is impossible.

There exists for each vapor a state of density which it cannot pass without losing its gaseous condition, and becoming liquid; this point is called

the condition of maximum density. When a volatile liquid is introduced in sufficient quantity into a vacuum, this condition is always reached, and then evaporation ceases. Any attempt to increase the density of this vapor by compressing it into a smaller space will be attended by the liquefaction of a portion, the density of the remainder being unchanged. If a little ether be introduced into a barometer, and the latter slowly sunk into a very deep cistern of mercury (fig. 42), it will be found that the height of the column of mercury in the tube above that in the cistern remains unaltered until the upper extremity of the barometer approaches the surface of the metal in the column and all the ether has become liquid. It will be observed also, that, as the tube sinks, the stratum of liquid ether increases in thickness, but no increase of elastic force occurs in the vapor above it, and, consequently, no increase of density; for tension and density are always, under ordinary circumstances at least, directly proportionate to each other.

Fig. 42.



The point of maximum density of vapor is dependent upon the temperature; it increases rapidly as the temperature rises. This is well shown in the case of water. Thus, taking the spec. grav. of atmospheric air at 100° =1000, that of aqueous vapor in its greatest state of compression for the temperature will be as follows:

Temperature. C.	F.	Specific gravity.	Weight of 100 cubic inches.
0°	32°	5·690	0·136 grains.
10	50	10·293	0·247 "
15·5	60	14·108	0·338 "
37·7	100	46·500	1·113 "
65·5	150	170·293	4·076 "
100	212	625·000	14·962 "

The last number was experimentally found by Gay-Lussac; the others are calculated from that by the aid of Dalton's table of tensions, on the assumption that steam, not in a state of saturation, that is, below the point of greatest density, obeys the laws of Mariotte (which is, however, only approximately true), and that when it is cooled it contracts like the permanent gases.

Thus, there are two distinct methods by which a vapor may be reduced to the liquid form — *pressure*, by causing increase of density until the point of maximum density for a given temperature is reached; and *cold*, by which the point of maximum density is itself lowered. The most powerful effects are produced when both are conjoined.

For example, if 100 cubic inches of vapor of water at 100° F., in the state above described, had its temperature reduced to 50° F., not less than 0·89* grain of liquid water would necessarily separate, or very nearly eight-tenths of the whole.

Evaporation into a space filled with air or gas follows the same law as evaporation into a vacuum: as much vapor arises, and the condition of maximum density is assumed in the same manner, as if the space were perfectly empty; the sole difference lies in the length of time required.

* 100 cub. inch. aqueous vapor at 100° F., weighing 1·113 grain, would at 50° F. become reduced to 91·07 cub. inch., weighing 0·225 grain.

When a liquid evaporates into a vacuum, the point of greatest density is attained at once, while in the other case some time elapses before this happens: the particles of air appear to oppose a sort of mechanical resistance to the rise of the vapor. The ultimate effect is, however, precisely the same.

When to a quantity of perfectly dry gas confined in a vessel closed by mercury a little water is added, the latter immediately begins to evaporate, and after some time as much vapor will be found to have risen from it as if no gas had been present, the quantity depending entirely on the temperature to which the whole is subjected. The tension of this vapor will add itself to that of the gas, and produce an expansion of volume, which will be indicated by an alteration of level in the mercury.

Vapor of water exists in the atmosphere at all times and in all situations, and there plays a most important part in the economy of nature. The proportion of aqueous vapor present in the air is subject to great variation, and it often becomes important to determine its quantity. This is easily done by the aid of the foregoing principles.

Dew-Point. — If the aqueous vapor be in its condition of greatest possible density for the temperature, or, as it is frequently, but most incorrectly, expressed, the air be saturated with vapor of water, the slightest reduction of temperature will cause the deposition of a portion in the liquid form. If, on the contrary, as is almost always in reality the case, the vapor of water be *below* its state of maximum density, that is, in an expanded condition, it is clear that a considerable fall of temperature may occur before liquefaction commences. The degree at which this takes place is called the dew-point, and it is determined with great facility by a very simple method. A little cup of thin tin plate or silver, well polished, is filled with water at the temperature of the air, and a delicate thermometer inserted. The water is then cooled by dropping in fragments of ice, or dissolving in it powdered sal-ammoniac, until moisture begins to make its appearance on the outside, dimming the bright metallic surface. The temperature of the dew-point is then read off upon the thermometer, and compared with that of the air.

Suppose, by way of example, that the latter were 70° F., and the dew-point 50° F., the elasticity of the watery vapor present would correspond to a maximum density proper to 50° F., and would support a column of mercury 0·375 inch high. If the barometer on the spot stood at 30 inches, therefore, 29·625 inches would be supported by the pressure of the dry air, and the remaining 0·375 inch by the vapor. Now a cubic foot of such a mixture must be looked upon as made up of a cubic foot of dry air, and a cubic foot of watery vapor, occupying the same space, and having tensions indicated by the numbers just mentioned. A cubic foot, or 1728 cubic inches of vapor, at 70° F., would become reduced by contraction, according to the usual law, to 1662·8 cubic inches at 50° F.; this vapor would be at its maximum density, having the specific gravity pointed out in the table; hence 1662·8 cubic inches would weigh 4·11 grains. The weight of the aqueous vapor contained in a cubic foot of air will thus be ascertained. In this country the difference between the temperature of the air and the dew-point seldom reaches 30° F. (16·6° C.) degrees; but in the Deccan, with a temperature of 90° F. (32·2° C.), the dew-point sinks as low as 29° F., making the degrees of dryness 61° F.*

Another method of finding the proportion of moisture present in the air is to observe the rapidity of evaporation, which is always in some relation to the degree of dryness. The bulb of a thermometer is covered with muslin, and kept wet with water; evaporation produces cold, as will presently be seen, and accordingly the thermometer soon sinks below the actual tem-

* Daniell, Introduction to Chemical Philosophy, p. 154.

perature of the air. When it comes to rest, the degree is noticed, and from a comparison of the two temperatures an approximation to the dew-point can be obtained by the aid of a mathematical formula contrived for the purpose. This is called the wet-bulb hygrometer: it is often made in the manner shown in fig. 43, where one thermometer serves to indicate the temperature of the air, and the other to show the rate of evaporation, being kept wet by the thread dipping in the water reservoir.

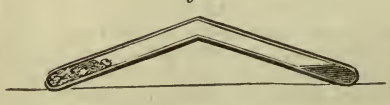
Fig. 43.

Liquefaction of Gases. — The perfect resemblance in every respect which vapors bear to permanent gases, led, very naturally, to the idea that the latter might, by the application of suitable means, be made to assume the liquid condition, and this surmise was, in the hands of Mr. Faraday, to a great extent verified. Out of the small number of such substances tried, not less than eight gave way; and it is quite fair to infer that, had means of sufficient power been at hand, the rest would have shared the same fate, and proved to be nothing more than the vapors of volatile liquids in a state very far removed from that of their maximum density. The subjoined table represents the results of Mr. Faraday's first investigations, with the pressure in atmospheres, and the temperatures at which the condensation takes place.*

	Atmospheres.	Temperatures. C.	Temperatures. F.
Sulphur dioxide	2	7·2°	45°
Hydrogen sulphide	17	10	50
Carbon dioxide	36	0	32
Chlorine	4	15·5	60
Nitrogen monoxide	50	7·2	45
Cyanogen	3·6	7·2	45
Ammonia	6·5	10	50
Hydrochloric acid	40	10	50

The method of proceeding was very simple: the materials were sealed up in a strong, narrow tube, together with a little pressure-gauge, consisting of a slender tube, closed at one end, and having within it, near the open extremity, a globule of mercury. The gas being disengaged by heat, accumulated in the tube, and by its own pressure brought about condensation. The force required for this purpose was judged of by the diminution of volume of the air in the gauge.

Fig. 44.



Mr. Faraday has since resumed, with the happiest results, the subject of the liquefaction of the permanent gases. By using narrow green glass tubes of great strength, powerful condensing syringes. and an extremely low temperature, produced by means to be presently described, olefiant gas, hydriodic and hydrobromic acids, phosphoretted hydrogen, and the gaseous fluorides of silicon and boron, were successively liquefied. Oxygen, hydrogen, nitrogen, nitrogen dioxide, carbon monoxide, and marsh gas, refused to liquefy at —166° F., while subjected to pressures varying from 27 to 58 atmospheres.

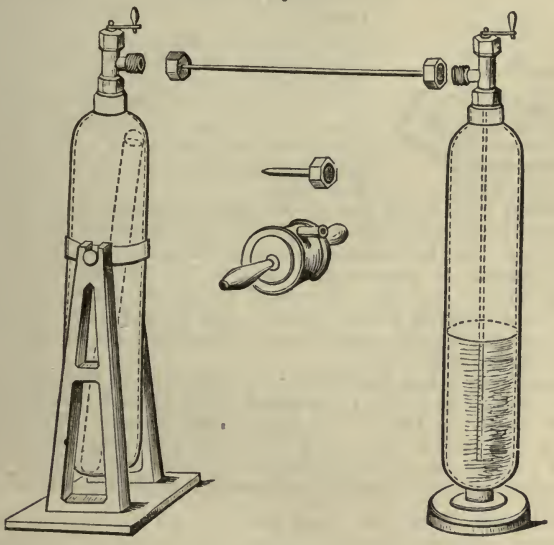
Sir Isambard Brunel, and, more recently, M. Thilorier, of Paris, succeeded

* Phil. Trans. for 1823, p. 189.

in obtaining liquid carbon dioxide (commonly called carbonic acid) in great abundance. The apparatus of M. Thilorier consists of a pair of extremely strong metallic vessels, one of which is destined to serve the purpose of a retort, and the other that of a receiver. They are made either of thick cast iron or gun-metal, or, still better, of the best and heaviest boiler-plate, and are furnished with stop-cocks of a peculiar kind, the workmanship of which must be excellent. The generating vessel or retort has a pair of trunnions upon which it swings in an iron frame. The joints are secured by collars of lead, and every precaution taken to prevent leakage under the enormous pressure the vessel has to bear. The receiver resembles the retort in every respect; it has a similar stop-cock, and is connected with the retort by a strong copper tube and a pair of union screw-joints; a tube passes from the stop-cock downwards, and terminates near the bottom of the vessel.

The operation is thus conducted: $2\frac{3}{4}$ lb. of acid sodium carbonate, and $6\frac{1}{4}$ lb. of water at 100° F., are introduced into the generator; oil of vitriol to the amount of $1\frac{1}{2}$ lb. is poured into a copper cylindrical vessel, which is

Fig. 45.



lowered down into the mixture, and set upright; the stop-cock is then screwed into its place, and forced home by a spanner and mallet. The machine is next tilted up on its trunnions, that the acid may run out of the cylinder and mix with the other contents of the generator; and this mixture is favored by swinging the whole backward and forward for a few minutes, after which it may be suffered to remain a little time at rest.

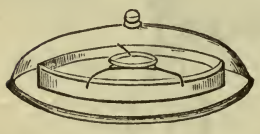
The receiver, surrounded with ice, is next connected with the generator, and both cocks opened; the liquefied carbon dioxide distils over into the colder vessel, and there again in part condenses. The cocks are now closed, the vessels disconnected, the cock of the generator opened to allow the contained gas to escape; and, lastly, when the issue of gas *has quite ceased*, the stop-cock itself is unscrewed, and the sodium sulphate turned

out. This operation must be repeated five or six times before any very considerable quantity of liquefied carbon dioxide will have accumulated in the receiver. When the receiver thus charged has its stop-cock opened, a stream of the liquid is forcibly driven up the tube by the elasticity of the gas contained in the upper part of the vessel.

The experimenter incurs great personal danger in using this apparatus, unless the utmost care be taken in its management. A dreadful accident occurred in Paris by the bursting of one of the iron vessels.

Liquid carbon dioxide is also very frequently prepared by means of an apparatus constructed by M. Natterer, of Vienna, which enables the experimentalist to work with less risk. The gas disengaged by means of sulphuric acid from acid potassium carbonate, is pumped by means of a force-pump into a wrought-iron vessel, exactly as the air is pumped into the receiver of an air-gun. When a certain pressure has been reached, the gas is liquefied, and if the pumping be continued, considerable quantities of the liquid carbon dioxide may be thus obtained. By this apparatus nitrous oxide gas has been condensed to a liquid without the use of frigorific mixtures.

Fig. 46.

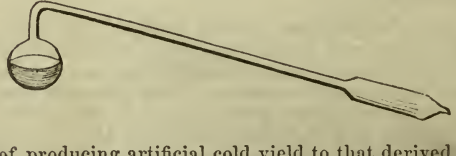


The cold produced by evaporation has been already adverted to: it is simply an effect arising from the conversion of sensible heat into latent by the rising vapor, and it may be illustrated in a variety of ways. Ether dropped on the hand thus produces the sensation of great cold; and water contained in a thin glass tube, surrounded by a bit of rag, is speedily frozen when the rag is kept wetted with ether.

When a little water is put into a watch-glass, supported by a triangle of wire over a shallow glass dish of sulphuric acid placed on the plate of a good air-pump, the whole covered with a low receiver, and the air withdrawn as perfectly as possible, the water is in a few minutes converted into a solid mass of ice. The absence of the impediment of the air, and the rapid absorption of watery vapor by the oil of vitriol, induce such quick evaporation that the water has its temperature almost immediately reduced to the freezing-point.

The same fact is shown by Wollaston's *cryophorus*, or frost-carrier. It is a glass vessel of the figure represented in fig. 47, and contains a small quantity of water, the rest of the space being vacuous. When all the water is turned into the bulb, and the empty extremity plunged into a mixture of ice and salt, the solidification of the vapor gives rise to so quick an evaporation from the surface of the water, that the latter freezes.

Fig. 47.

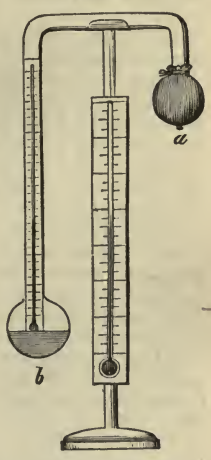


All means of producing artificial cold yield to that derived from the evaporation of the liquefied carbon dioxide just mentioned. When a jet of that liquid is allowed to issue into the air from a narrow aperture, so intense a degree of cold is produced by the evaporization of a part, that the remainder freezes to a solid, and falls in a shower of snow. By suffering this jet of liquid to flow into a metal box provided for the purpose, shown in

fig. 45, a large quantity of the solid oxide may be obtained: it closely resembles snow in appearance, and when held in the hand occasions a painful sensation of cold, while it gradually disappears. When it is mixed with a little ether, and poured upon a mass of mercury, the latter is almost instantly frozen, and in this way pounds of the solidified metal may be obtained. The addition of the ether facilitates the contact of the carbon dioxide with the mercury.

The temperature of a mixture of solid carbon dioxide and ether in the air, measured by a spirit-thermometer, was found to be—106° F.; when the same mixture was placed beneath the receiver of an air-pump, and exhaustion rapidly made, the temperature sank to —166° F. This was the method of obtaining extreme cold employed by Mr. Faraday in his last experiments on the liquefaction of gases. Under such circumstances the liquefied hydriodic and hydrobromic acids, sulphur dioxide, carbon dioxide, nitrogen monoxide, hydrogen sulphide, cyanogen, and ammonia, froze to colorless transparent *solids*, and alcohol became thick and oily.

Fig. 48.



The principle of the cryophorus has been very happily applied by Mr. Daniell to the construction of a dew-point hygrometer, fig. 48. It consists of a bent glass tube terminated by two bulbs, one of which is half filled with ether, the whole being vacuous as respects atmospheric air. A delicate thermometer is contained in the longer limb, the bulb of which dips into the ether; a second thermometer on the stand serves to show the actual temperature of the air. The upper bulb is covered with a bit of muslin. When an observation is to be made, the liquid is all transferred to the lower bulb, and ether dropped upon the upper one, until by the cooling effect of evaporation a distillation of the contained liquid takes place from one part of the apparatus to the other, by which such a reduction of temperature of the ether is brought about that dew is deposited on the outside of the bulb, which is made of black glass in order that it may be more easily seen. The difference of temperature indicated by the two thermometers is then read off.

SPECIFIC HEAT.

It is a very remarkable fact that equal weights of different substances having the same temperature require different amounts of heat to raise them to a given degree of temperature. If 1 lb. of water, at 100°, be mixed with 1 lb. at 40°, then, as is well known, a mean temperature of $\frac{100 + 40}{2} = 70$ is obtained. In the same way the mean temperature is found when warm and cold oil, or warm and cold mercury, &c., are mixed together. But if 1 lb. of water at 100° be mixed with 1 lb. of olive oil at 40°, or with 1 lb. of mercury at 40°, then instead of the mean temperature of 70°, in the one case 80°, in the other case 98°, will be obtained: 20 degrees of heat, which the water (by cooling from 100° to 80°) gave to the same weight of oil, were sufficient to raise the oil 40°, that is, from 40° to 80°; and 2°, which the water lost by cooling from 100° to 98°, sufficed to heat an equal quantity of mercury 58°, namely, from 40° to 98°.

It is evident from these experiments that the quantities of heat which equal weights of water, olive oil, and mercury, require to raise their temperature to the same height, are unequal, and that they are in the proportion of the numbers $1 : \frac{20}{40} : \frac{2}{58}$, or $1 : \frac{1}{2} : \frac{1}{29}$.

These quantities of heat, expressed relatively to the quantity of heat required to raise the temperature of an equal weight of water from 0° to 1° C., are called the *specific heats* of the various substances: thus the experiments just described show that the specific heat of olive oil is $\frac{1}{2}$, that is to say, the quantity of heat which would raise the temperature of any given quantity of olive oil from 0° to 1° would raise that of an equal weight of water only from 0° to $\frac{1}{2}$°, or of half that quantity of water from 0° to 1°.

The specific heats of bodies are sometimes said to measure their relative *capacities for heat.*

There are three distinct methods by which the specific heats of various substances may be estimated. The first of these is by observing the quantity of ice melted by a given weight of the substance heated to a particular temperature; the second is by noting the time which the heated body requires to cool down through a certain number of degrees; and the third is the method of mixture, on the principle illustrated: this latter method is preferred as the most accurate.

The determination of the specific heat of different substances has occupied the attention of many experimenters; among these, Dulong and Petit, and recently Regnault and Kopp, deserve especial mention.

From the observation of these and other physicists, it follows that each body has its peculiar specific heat, and that the specific heat increases with increase of temperature. If, for example, the heat which the unit of water loses by cooling from 10° to 0° be marked at 10°, then the loss by cooling from 50° to 0° will be, not 50, corresponding to the difference of temperature, but 50·1. By cooling from 100° to 0° it is 100·5, and rises to 203·2 when the water is heated under great pressure to 200° and afterwards cooled to 0°. Similar and even more striking differences have been found with other substances. It has also been proved that the specific heat of any substance is greater in the liquid than in the solid state. For example, the specific heat of ice is 0·504, that is, not more than half as great as that of liquid water.

It is remarkable that the specific heat of water is greater than that of all other solid and liquid substances, and is only exceeded by that of hydrogen. The specific heat of the solid parts of the crust of the globe is on an average $\frac{1}{4}$, and that of an atmosphere nearly $\frac{1}{4}$ that of water.

If the specific heat of any body within certain degrees of temperature be accurately known, then from the quantity of heat which this body gives out when quickly dipped into cold water, the temperature to the which the body was heated may be determined. Pouillet has founded on this fact a method of measuring high temperatures, and for this purpose, with the help of the air-thermometer, he has determined the specific heat of platinum up to 1600°.

The determination of the specific heat of gases is attended with peculiar difficulties, on account of the comparatively large volume of small weights of gases. For many gases, however, satisfactory results have been obtained by the method of mixing.

When a gas expands, heat becomes latent. The amount of heat required, therefore, to raise a gas to any given temperature increases the more the gas in question is allowed to expand. The quantity of heat which the unit-weight of a gas requires in order to raise its temperature 1° without its volume undergoing any change (which can only take place by the pressure being simultaneously augmented) is called the specific heat of the

gas *at constant volume.* The quantity of heat required by the unit-weight of a gas to raise its temperature 1°, it being at the same time allowed to dilate to such an extent that the pressure to which it is exposed remains unchanged, is called the specific heat of the gas *at constant pressure.* According to what has already been stated, the specific heat at constant pressure must be greater than that at constant volume. Dulong found, in the case of atmospheric air, of oxygen, of hydrogen, and of nitrogen, that the two specific heats are in the proportion 1·421 : 1. For carbon monoxide, however, he obtained the proportion of 1·423, for carbon dioxide 1·337, for nitrogen dioxide 1·343, and for olefiant gas 1·24 to 1. The exact determination of these ratios is extremely difficult, and the results of different physicists by no means agree.

The first satisfactory comparison of the specific heat of air with that of water was made by Count Rumford; later comparisons of the specific heat of various gases have been made by Delaroche and Berard, Dulong and Regnault.

The first researches of Delaroche and Berard furnished the results embodied in the following table: —

SPECIFIC HEAT.

	Equal volumes.		Equal weights.	
	The volumes constant.	The pressure constant.	Air = 1.	Water = 1.
Atmospheric air	1	1	1	0·2669
Oxygen	1	1	0·9045	0·2414
Hydrogen	1	1	14·4510	3·8569
Nitrogen	1	1	1·0295	0·2748
Carbon monoxide	1	1	1·0337	0·2759
Nitrogen monoxide	1·227	1·160	0·7607	0·2030
Carbon dioxide	1·249	1·175	0·7685	0·2051
Olefiant gas	1·754	1·531	1·5829	0·4225

The latest and most trustworthy determinations are those of Regnault, which are given in the subjoined table. Its second column of figures, headed "For equal weights. Water = 1," contains the specific heats of the gases under constant pressure, that of water being taken equal to 1. As it is both useful and interesting to compare the quantities of heat which gases, having equal volumes at 0° and 760 mm., require to raise them 1°, the pressure remaining constant, they have been given under the head "For equal volumes" in the third column of the table, wherein, it should be stated, the unit of heat is the amount of heat required to heat a unit-weight of water 1°, while the unit of volume is the volume of a unit-weight of air at 0° and 760 mm. The first column gives the specific gravity of the gases referred to air as 1.

SPECIFIC HEAT AT CONSTANT PRESSURE.

Gases.	Specific Gravity. Air = 1.	For equal weights. Water = 1.	For equal volumes.
Atmospheric air	1	0·2377	0·2377
Oxygen	1·1056	0·2175	0·2405
Nitrogen	0·9713	0·2438	0·2368
Hydrogen	0·0692	3·4090	0·2359
Chlorine	2·4502	0·1210	0·2965
Bromine vapor	5·4772	0·0555	0·3040
Carbon monoxide	0·9670	0·2450	0·2370
Carbon dioxide	1·5210	0·2169	0·3307

Gases.	Specific Gravity. Air = 1.	For equal weights. Water = 1.	For equal volumes.
Nitrogen monoxide	1·5241	0·2262	0·3447
Nitrogen dioxide	1·0384	0·2317	0·2406
Olefiant gas	0·9672	0·4040	0·4106
Marsh gas	0·5527	0·5929	0·3277
Aqueous vapor	0·6220	0·4805	0·2989
Sulphuretted hydrogen	1·1746	0·2432	0·2857
Sulphur dioxide	2·2112	0·1544	0·3414
Vapor of carbon bisulphide	2·6258	0·1569	0·4122
Hydrochloric acid	1·2596	0·1852	0·2333
Ammonia	0·5894	0·5084	0·2996

The researches of Delaroche and Berard led them to suppose that the specific heat of gases increased rapidly as the temperature was raised, and that for a given volume of gas it increased in proportion to the density or tension of the gas. Regnault found, however, the quantity of heat which a given volume of gas requires to raise it to a certain temperature, to be independent of its density; and that for each degree between — 30° and 225° it is constant. Carbon dioxide, however, forms an exception to this rule, its specific heat increasing with the temperature. Regnault believes that other gases agree with carbon dioxide in showing this anomaly, but he has not established it by experiment. In the table, mean values for temperatures between 10° and 200° have been given.

Several physicists have held that the specific heats of elementary gases, referred to equal volumes, are identical. The numbers which Regnault found for chlorine and bromine, however, show that the law does not hold good for all elementary gases.

It has been already stated that, when a gas expands, heat becomes latent. If a gas on expanding be not supplied with the requisite heat, its temperature falls on account of its own free heat becoming latent. On the other hand, if a gas be compressed, this latent heat becomes free, and causes an elevation of temperature, which, under favorable circumstances, may be raised to ignition: syringes by which tinder is kindled are constructed on this principle.

Dulong and Petit observed in the course of their investigation a most remarkable circumstance. If the specific heats of bodies be computed upon equal weights, numbers are obtained all different, and exhibiting no simple relations among themselves; but if, instead of equal weights, quantities be taken in the proportion of the atomic weights, an almost perfect coincidence in the numbers will be observed, showing that some exceeding intimate connection must exist between the relations of bodies to heat and their chemical nature; and when the circumstance is taken into view, that relations of even a still closer kind link together chemical and electrical phenomena, it is not too much to expect that ere long some law may be discovered far more general than any with which we are yet acquainted.

In the following table the elementary bodies are arranged nearly in the order of their specific heats, as determined by Regnault, beginning with those whose specific heat is the greatest; and this order, it will be observed, is the inverse of that of the atomic weights in the third column: —

Specific Heats of Elementary Bodies.

Elements.	Specific Heat (that of Water=1).	Atomic Weights.	Product of Sp. Heat × At. Weight.
Lithium	0·9408	7	6·59
Sodium	0.2934	23	6·75
Aluminium	0·2143	27.5	5·89
Phosphorus { liquid	0·2120	31	6·57
Phosphorus { solid	0·1887	31	5·85
Sulphur	0·2026	32	6·48
Potassium	0·1696	39	6·61
Iron	0·1138	56	6·37
Nickel	0·1086	58·7	6·37
Cobalt	0·1070	58·7	6·28
Copper	0·9515	63·5	6·04
Zinc	0·9555	65	6·24
Arsenic	0·8140	75	6·10
Selenium	0·7616	79	6·02
Bromine (solid)	0·8432	80	6·75
Palladium	0·5928	106·5	6·31
Silver	0·5701	108	6·16
Cadmium	0·5669	112	6.35
Tin	0·5623	118	6·63
Antimony	0·5077	122	6·19
Iodine	0·5412	127	6·87
Tellurium	0·4737	128	6·06
Gold	0·3242	196·7	6·38
Platinum	0·3113	197·4	6·15
Mercury { solid	0·3192	200	6·38
Mercury { liquid	0·3332	200	6·66
Lead	0·3140	207	6·50
Bismuth	0·3084	210	6·48

A comparison of the numbers in the fourth column of this table shows that for a considerable number of elementary bodies in the solid state the specific heats are very nearly proportional to the atomic weights, so that the products of the specific heats of the elements into their atomic weights give nearly a constant quantity, the mean value being 6·4. This quantity may be taken to represent the *atomic heat* of the several elements in the solid state, or the quantity of heat which must be imparted to or removed from atomic proportions of the several elements, in order to produce equal variations of temperature.

Nevertheless, this law must not be understood as perfectly general, for there are three elements, namely, carbon, boron, and silicon, which exhibit decided exceptions to it, as shown by the following numbers:

Elements.	Specific Heat.	Atomic Weights.	Product of Sp. Heat × At. Weight.
Boron, crystallized .	0·2500	11	2·75
Carbon { wood charcoal	0·2415	12	2·90
Carbon { graphite .	0·2008	12	2·41
Carbon { diamond . .	0·1469	12	1·76
Silicon { crystallized .	0·1774	28	4·97
Silicon { fused . .	0·1750	28	4·70

The specific heats and molecular weights of similarly constituted compounds exhibit, for the most part, the same relation as that which is observed between the specific heats and atomic weights of the elements.

SOURCES OF HEAT.

The first and greatest source of heat, compared with which all others are totally insignificant, is the sun. The luminous rays are accompanied by rays of a heating nature, which, striking against the surface of the earth, elevate its temperature; this heat is communicated to the air by convection, as already described, air and gases in general not being sensibly heated by the passage of the rays.

A second source of heat is supposed to exist in the interior of the earth. It has been observed that in sinking mine-shafts, boring for water, &c., the temperature rises in descending, at the rate, it is said, of about $\frac{5}{9}$° C. (1° F.) for every 45 feet, or 65° C. (117° F.) per mile. On the supposition that the rise continues at the same rate, the earth, of the depth of less than two miles, would have the temperature of boiling water; at nine miles it would be red-hot; and at 30 or 40 miles depth all known substances would be in a state of fusion.*

According to this idea, the earth must be looked upon as an intensely heated fluid spheroid, covered with a crust of solid badly conducting matter, cooled by radiation into space, and bearing somewhat the same proportions in thickness to the ignited liquid within, that the shell of an egg bears to its fluid contents. Without venturing to offer any opinion on this theory, it may be sufficient to observe that it is not positively at variance with any known fact; that the figure of the earth is really such as would be assumed by a fluid mass; and, lastly, that it offers the best explanation we have of the phenomena of hot springs and volcanic eruptions, and agrees with the chemical nature of their products.

Among the other sources of heat are chemical combination and mechanical work.

The disengagement of heat in the act of combination is a phenomenon of the utmost generality. The quantity of heat given out in each particular case is fixed and definite; its intensity is dependent upon the time over which the action is extended. Many admirable researches on this subject have been published; but their results will be more advantageously considered at a later part of this work, in connection with the laws of chemical combination.

* The Artesian well at Grenelle, near Paris, has a depth of 1794·5 English feet; it is bored through the chalk basin to the sand beneath. The temperature of the water, which is exceedingly abundant, is 82° F.; the mean temperature of Paris is 51° F.; the difference is 31° F.; which gives a rate of about 1° for 58 feet.

Heat produced by Mechanical Work.—Heat and motion are convertible one into the other. The powerful mechanical effects produced by the elasticity of the vapor evolved from heated liquids afford abundant illustration of the conversion of heat into motion; and the production of heat by friction, by the hammering of metals, and in the condensation of gases (p. 72), shows with equal clearness that motion may be converted into heat.

In some cases the rise of temperature thus produced appears to be due to a diminution of heat-capacity in the body operated upon, as in the case of a compressed gas just alluded to. Malleable metals, also, as iron and copper, which become heated by hammering or powerful pressure, are found thereby to have their density sensibly increased and their capacity for heat diminished. A soft iron nail may be made red-hot by a few dexterous blows on an anvil; but the experiment cannot be repeated until the metal has been *annealed*, and in that manner restored to its former physical state.

But the amount of heat which can be developed by mechanical force is, in most cases, out of all proportion to what can be accounted for in this way. Sir H. Davy melted two pieces of ice by rubbing them together in a vacuum at the temperature of 0°; and Count Rumford found that the heat developed by the boring of a brass cannon was sufficient to bring to the boiling-point two and a half gallons of water, while the dust or shavings of metal, cut by the borer, weighed only a few ounces. In these and all similar cases the heat appears as a direct result of the force expended; the motion is converted into heat.

The connection between heat and mechanical force appears still more intimate when it is shown that they are related by an exact numerical law, a given quantity of the one being always convertible into a definite amount of the other. The first approximate determination of this most important numerical relation was made by Count Rumford in the manner just alluded to. A brass cylinder enclosed in a box containing a known weight of water at 60° F. was bored by a steel borer made to revolve by horse-power, and the time was noted which elapsed before the water was raised to the boiling-point by the heat resulting from the friction. In this manner it was found that the heat required to raise the temperature of a pound of water by 1° F. is equivalent to 1034 times the force expended in raising a pound weight one foot high, or to 1034 "foot pounds," as it is technically expressed. This estimate is now known to be too high, no account having been taken of the heat communicated to the containing vessel, or of that which was lost by dispersion during the experiment.

For the most exact determinations of the mechanical equivalent of heat we are indebted to the careful and elaborate researches of Mr. J. P. Joule. From experiments made in the years 1840–43 on the relations between the heat and mechanical power generated by the electric current, Mr. Joule was led to conclude that the heat required to raise the temperature of a pound of water 1° F. is equivalent to 838 foot-pounds; this he afterwards reduced to 772; and a nearly equal result was afterwards obtained by experiments on the condensation and rarefaction of gases; but this estimate has since been found to be likewise too great.

The most trustworthy results are obtained by measuring the quantity of heat generated by the friction between solids and liquids. It was for a long time believed that no heat was evolved by the friction of liquids and gases. But in 1842 Meyer showed that the temperature of water may be raised 22° or 23° F. by agitating it. The warmth of the sea after a few days of stormy weather is also probably an effect of fluid friction.

The apparatus employed by Mr. Joule for the determination of this important constant, by means of the friction of water, consisted of a brass paddle-wheel furnished with eight sets of revolving vanes, working between four sets of stationary vanes. This revolving apparatus, of which fig. 49

shows a vertical, and fig. 50 a horizontal section, was firmly fitted into a copper vessel (see fig. 51) containing water, in the lid of which were two necks, one for the axis to revolve in without touching, the other for the insertion of a thermometer. A similar apparatus, but made of iron, and of smaller size, having six rotatory and eight sets of stationary vanes, was used for the experiments on the friction of mercury. The apparatus for the friction of cast-iron consisted of a vertical axis carrying a bevelled cast-iron wheel, against which a bevelled wheel was pressed by a lever. The wheels were enclosed in a cast-iron vessel filled with mercury, the axis passing through the lid. In each apparatus motion was given to the axis by the descent of leaden weights *w* (fig. 51) suspended by strings from the axis of two wooden pulleys, one of which is

Fig. 49.

Fig. 50.

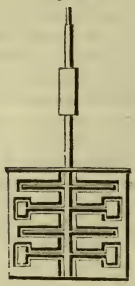
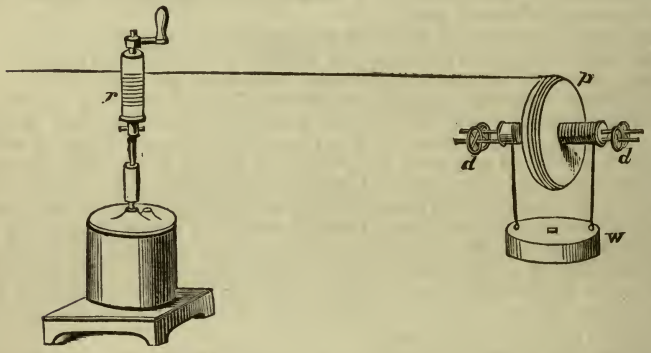


Fig. 51.



shown at *p*, their axis being supported on friction wheels *d d*, and the pulleys were connected by fine twine with a wooden roller *r*, which, by means of a pin, could be easily attached to or removed from the friction apparatus.

The mode of experimenting was as follows: — The temperature of the frictional apparatus having been ascertained, and the weights wound up, the roller was fixed to the axis, and the precise height of the weights ascertained; the roller was then set at liberty, and allowed to revolve till the weights touched the floor. The roller was then detached, the weights wound up again, and the friction renewed. This having been repeated twenty times, the experiment was concluded with another observation of the temperature of the apparatus. The mean temperature of the apartment was ascertained by observations made at the beginning, middle, and end of each experiment. Corrections were made for the effects of radiation and conduction; and, in the experiments with water, for the quantities of heat absorbed by the copper vessel and the paddle-wheel. In the experiments with mercury and cast-iron, the heat-capacity of the entire apparatus was ascertained by observing the heating effect which it produced on a known quantity of water in which it was immersed. In all the ex-

periments, corrections were also made for the velocity with which the weights came to the ground, and for the friction and rigidity of the strings. The thermometers used were capable of indicating a variation of temperature as small as $\frac{1}{200}$ of a degree Fahrenheit.

The following table contains a summary of the results obtained by this method; the second column gives the results as they were obtaine in air; in the third column the same results corrected for a vacuum: —

Material employed.	Equivalent in air.	Equivalent in vacuo.	Mean.
Water . .	773·640	772·692	772·692
Mercury . .	773·762 776·303	772·814 775·352	774·083
Cast-iron . .	776·997 774·880	776·045 774·930	774·987

In the experiments with cast-iron, the friction of the wheels produced a considerable vibration in the frame-work of the apparatus, and a loud sound; it was therefore necessary to make allowance for the quantity of force expended in producing these effects. The number 772·692, obtained by the friction of water, is regarded as the most trustworthy; but even this may be a little too high; because even in the friction of fluids it is impossible entirely to avoid vibration and sound. The conclusions deduced from these experiments are: —

1. *That the quantity of heat produced by the friction of bodies, whether solid or liquid, is always proportional to the force expended.*

2. *That the quantity of heat capable of increasing the temperature of* 1*lb. of water (weighed in vacuo, and between* 55° *and* 60°) *by* 1° *F., requires for its evolution the expenditure of a mechanical force represented by the fall of* 772*lbs. through the space of* 1 *foot.*

Or, the heat capable of increasing the temperature of 1 *gram of water by* 1° *C., is equivalent to a force represented by the fall of* 423·55 *grams through the space of* 1 *metre. This is consequently the effect of "a unit of heat."*

Experiments made by other philosophers on the work done by a steam-engine, on the heat evolved by an electro-magnetic engine at rest and in motion, and on the heat evolved in the circuit of a voltaic battery and in a metallic wire through which an electric current is passing, have given values for the mechanical equivalent of heat very nearly equal to the above.

DYNAMICAL THEORY OF HEAT.

For a very long time two rival theories have been held regarding the nature of heat: on the one hand, heat has been viewed as having a material existence, though differing from ordinary matter in being without weight, and in other respects; on the other hand, it has been regarded as a state or condition of ordinary matter, and generally as a condition of motion. From the latter part of the last century, until the modern researches upon the mechanical equivalent, the former view had by far the greater number of adherents. Its popularity may be chiefly traced to the teaching of Black and Lavoisier. By the former of these philosophers, the various capacities for heat, or specific heats of different bodies, seem to have been regarded as analogous to the various proportions of the same acid required to neutralize equal quantities of different bases, while the solid, liquid, and gaseous states were explained by Black as representing so many distinct proportions in which heat was capable of combining with ordinary matter. Very similar views were advocated by Lavoisier: he regarded all gases as compounds of a base characteristic of each, with *caloric*, and supposed that when, as the result of chemical action, they assumed the liquid or solid state, this caloric was set free and appeared as sensible heat.

Heat was compared by these philosophers to a material substance, in order to explain its then known quantitative relations; and from this point of view the conception introduced by them had the great advantage of being more easily grasped than any which the advocates of the immaterial nature of heat had to offer in its place. It was much easier to conceive of definite quantities of an exceedingly subtile substance or fluid, than of definite quantities of motion, which was itself undefined as to its nature. It was a direct consequence of the material view, that heat should be considered as indestructible and as incapable of being produced, and therefore that the total quantity of heat in the universe should be regarded as at all times the same.

But, on the other hand, this hypothesis did not afford a satisfactory explanation of the production of heat by mechanical means. Here it was not easy to deny the actual generation of heat, or to explain the effects as depending merely on its altered distribution. Nevertheless, the evolution of heat by friction and percussion was generally considered, by the advocates of the material view, as in some way resulting from a diminution in the capacities for heat of the bodies operated upon; and this explanation derived considerable support from the remark, made by Black, that a piece of soft iron, which has been once made red-hot by hammering (see p. 75), cannot be so heated a second time until it has been heated to redness in a fire and allowed to cool. In this case, certainly, it seemed as though the hammering forced out heat from the mass of iron, like water from a sponge, and that a fresh supply was taken up when the iron was put in the fire. This explanation, however, did not satisfy Rumford, who, in the investigation described above, made direct experiments upon the specific heat of the chips of metal detached by the friction, and found it to be identical with that of brass under ordinary circumstances. Still more decisive proof that the heat generated by friction cannot be ascribed to a diminution of specific heat in the substances operated on was afforded by Davy's experiment on the liquefaction of ice by friction; for in this case the ice was converted into a liquid having twice the specific heat of the ice itself. Hence Davy* drew the conclusion that, "The immediate cause of the phenomena of heat is motion, and the laws of its communication are precisely the same as the laws of the communication of motion."

The mechanical, or dynamical theory, which regarded heat as consisting in a state of molecular motion, cannot however be said to have been definitely established, until it also was made quantitative, — until it was shown that exact numerical laws regulate the production of heat by work or of work by heat, equally with its production during solidification and disappearance during fusion.

To illustrate the general nature of the dynamical theory of heat, we give an outline of the view of the constitution of gases, first put forward, in its present form, by Joule;† and subsequently developed by Krönig,‡ and Clausius,§ and of the explanation of the relations existing between solids, liquids, and gases, which has been deduced from it by the last-named philosopher.

First, then, it is assumed that the particles of all bodies are in constant motion, and that this motion constitutes heat, the kind and quantity of motion varying according to the state of the body, whether solid, liquid, or gaseous.

In gases, the molecules — each molecule being an aggregate of atoms — are supposed to be constantly moving forward in straight lines, and with a

* Elements of Chemical Philosophy, 1812, pp. 94, 95.
‡ Pogg. Ann. xcix. 315.
† Ann. Ch. Phys. [3] l. 381.
§ *Ibid.* 353.

constant velocity, till they impinge against each other, or against an impenetrable wall. This constant impact of the molecules produces the expansive tendency or elasticity which is the peculiar characteristic of the gaseous state. The rectilinear movement is not, however, the only one with which the particles are affected. For the impact of two molecules, unless it takes place exactly in the line joining their centres of gravity, must give rise to a rotatory motion; and, moreover, the ultimate atoms of which the molecules are composed may be supposed to vibrate within certain limits, being, in fact, thrown into vibration by the impact of the molecules. This vibratory motion is called by Clausius, *the motion of the constituent atoms.* The total quantity of heat in the gas is made up of the progressive motion of the molecules, together with the vibratory and other motions of the constituent atoms; but the progressive motion alone, which is the cause of the expansive tendency, determines the *temperature.* Now, the outward pressure exerted by the gas against the containing envelope arises, according to the hypothesis under consideration, from the impact of a great number of gaseous molecules against the sides of the vessel. But at any given temperature, that is, with any given velocity, the number of such impacts taking place in a given time, must vary inversely as the volume of the given quantity of gas; hence *the pressure varies inversely as the volume or directly as the density*, which is Boyle's law.

When the volume of the gas is constant, the pressure resulting from the impact of the molecules is proportional to the sum of the masses of all the molecules multiplied into the squares of their velocities; in other words, to the so-called *vis viva* or *working force* of the progressive motion. If, for example, the velocity be doubled, each molecule will strike the sides of the vessel with a twofold force, and its number of impacts in a given time will also be doubled: hence the total pressure will be quadrupled.

Now, we know that when a given quantity of any perfect gas is maintained at a constant volume, it tends to expand by $\frac{1}{273}$ of its bulk at zero for each degree Centigrade. Hence the pressure or elastic force increases proportionally to the temperature reckoned from —273° C.; that is to say, to the absolute temperature. Consequently, the *absolute temperature is proportional to the working force of the progressive motion.*

Moreover, as the motions of the constituent particles of a gas depend on the manner in which its atoms are united, it follows that in any given gas the different motions must be to one another in a constant ratio; and, therefore, the *vis viva* or *working force* of the progressive motion must be an aliquot part of the entire working force of the gas: hence also the absolute temperature is proportional to the total working force arising from all the motions of the particles of the gas.

From this it follows that the quantity of heat which must be added to a gas of constant volume in order to raise its temperature by a given amount, is constant and independent of the temperature. In other words, the specific heat of a gas referred to a given volume is constant, a result which agrees with this experiments of Regnault, mentioned at p. 72. The result may be otherwise expressed, as follows: — *The total* or working force *of the gas is to the working force of the progressive motion of the molecules, which is the measure of the temperature, in a constant ratio.* This ratio is different for different gases, and is greater as the gas is more complex in its constitution: in other words, as its molecules are made up of a greater number of atoms. The specific heat referred to a constant pressure is known to differ from the true specific heat only by a constant quantity.

The relations just considered between the pressure, volume, and temperature of gases, presuppose, however, certain conditions of molecular constitution, which are, perhaps, never rigidly fulfiled; and, accordingly, the experiments of Magnus and Regnault show (p. 52) that gases do exhibit

slight deviations from Gay-Lussac and Boyle's laws. What the conditions are which strict adherence to these laws would require, will be better understood by considering the differences of molecular constitution which must exist in the solid, liquid, and gaseous states.

A movement of molecules must be supposed to exist in all three states. In the *solid state*, the motion is such that the molecules oscillate about certain positions of equilibrium, which they do not quit, unless they are acted upon by external forces. This vibratory motion may, however, be of a very complicated character. The constituent atoms of a molecule may vibrate separately; the entire molecules may also vibrate as such about their centres of gravity, and the vibrations may be either rectilinear or rotatory. Moreover, when extraneous forces act upon the body, as in shocks, the molecules may permanently alter their relative positions.

In the *liquid state* the molecules have no determinate positions of equilibrium. They may rotate completely about their centres of gravity, and may also move forward into other positions. But the repulsive action arising from the motion is not strong enough to overcome the mutual attraction of the molecules and separate them completely from each other. A molecule is not permanently associated with its neighbors, as in the solid state; it does not leave them spontaneously, but only under the influence of forces exerted upon it by other molecules, with which it then comes into the same relation as with the former. There exists, therefore, in the liquid state, a vibratory, rotatory, and progressive movement of the molecules, but so regulated, that they are not thereby forced asunder, but remain within a certain volume without exerting any outward pressure.

In the *gaseous* state, on the other hand, the molecules are removed quite beyond the sphere of their mutual attractions, and travel onward in straight lines according to the ordinary laws of motion. When two such molecules meet, they fly apart from each other, for the most part with a velocity equal to that with which they came together. The perfection of the gaseous state, however, implies: — 1. That the space actually occupied by the molecules of the gas be infinitely small in comparison with the entire volume of the gas. — 2. That the time occupied in the impact of a molecule, either against another molecule or against the sides of the vessel, be infinitely small in comparison with the interval between any two impacts. — 3. That the influence of the molecular forces be infinitely small. When these conditions are not completely fulfilled, the gas partakes more or less of the nature of a liquid, and exhibits certain deviations from Gay-Lussac and Boyle's laws. Such is, indeed, the case with all known gases; to a very slight extent with those which have not yet been reduced into the liquid state; but to a greater extent with vapors and condensable gases, especially near the points of condensation.

Let us now return to the consideration of the liquid state. It has been said that the molecule of a liquid, when it leaves those with which it is associated, ultimately takes up a similar position with regard to other molecules. This, however, does not preclude the existence of considerable irregularities in the actual movements. Now, at the surface of the liquid, it may happen that a particle, by a peculiar combination of the rectilinear, rotatory, and vibratory movements, may be projected from the neighboring molecules with such force as to throw it completely out of their sphere of action before its projectile velocity can be annihilated by the attractive force which they exert upon it. The molecule will then be driven forward into the space above the liquid, as if it belonged to a gas, and that space, if originally empty, will in consequence of the action just described, become more and more filled with these projected molecules, which will comport themselves within it exactly like a gas, impinging and exerting pressure upon the sides of the envelope. One of these sides, however, is formed by

the surface of the liquid, and when a molecule impinges upon this surface, it will, in general, not be driven back, but retained by the attractive forces of the other molecules. A state of equilibrium, not static, but dynamic, will therefore be attained, when the number of molecules projected in a given time into the space above, is equal to the number which in the same time impinge upon and are retained by the surface of the liquid. This is the process of vaporization. The density of the vapor required to insure the compenzation just mentioned, depends upon the rate at which the particles are projected from the surface of the liquid, and this again upon the rapidity of their movement within the liquid, that is to say, upon the temperature. It is clear, therefore, that the density of a saturated vapor must increase with the temperature.

If the space above the liquid is previously filled with a gas, the molecules of this gas will impinge upon the surface of the liquid, and thereby exert pressure upon it; but as these gas-molecules occupy but an extremely small proportion of the space above the liquid, the particles of the liquid will be projected into that space almost as if it were empty. In the middle of the liquid, however, the external pressure of the gas acts in a different manner. There also it may happen that the molecules may be separated with such force as to produce a small vacuum in the midst of the liquid. But this space is surrounded on all sides by masses which afford no passage to the disturbed molecules; and in order that they may increase to a permanent vapor-bubble, the number of molecules projected from the inner surface of the vessel must be such as to produce a pressure outwards equal to the external pressure tending to compress the vapor-bubble. The boiling of the liquid will, therefore, be higher as the external pressure is greater.

According to this view of the process of vaporization, it is possible that vapor may rise from a solid as well as from a liquid; but it by no means necessarily follows that vapor must be formed from all bodies at all temperatures. The force which holds together the molecules of a body may be too great to be overcome by any combination of molecular movements, so long as the temperature does not exceed a certain limit.

The *production* and *consumption of heat* which accompany changes in the state of aggregation, or of the volume of bodies, are easily explained, according to the preceding principles, by taking account of the *work* done by the acting forces. This work is partly *external* to the body, partly *internal.* To consider first the *internal* work:

When the molecules of a body change their relative positions, the change may take place either in accordance with or in opposition to the action of the molecular forces existing within the body. In the former case, the molecules, during the passage from one state to the other, have a certain velocity imparted to them, which is immediately converted into heat; in the latter case, the velocity of their movement, and consequently the temperature of the body, is diminished. In the passage from the solid to the liquid state, the molecules, although not removed from the spheres of their mutual attractions, nevertheless change their relative positions in opposition to the molecular forces, which forces have, therefore, to be overcome. In evaporation, a certain number of the molecules are completely separated from the remainder, which again implies the overcoming of opposing forces. In both cases, therefore, work is done, and a certain portion of the working force of the molecules, that is, of the heat of the body, is lost. But when once the perfect gaseous state is attained, the molecular forces are completely overcome, and any further expansion may take place without internal work, and, therefore, without loss of heat, provided there is no external resistance.

But in nearly all cases of change of state or volume, there is a certain amount of external resistance to be overcome, and a corresponding loss of

heat. When the pressure of a gas, that is to say, the impact of its atoms, is exerted against a movable obstacle, such as a piston, the molecules lose just so much of their moving power as they have imparted to the piston, and, consequently, their velocity is diminished and the temperature lowered. On the contrary, when a gas is compressed by the motion of a piston, its molecules are driven back with greater velocity than that with which they impinged on the piston, and, consequently, the temperature of the gas is raised.

When a liquid is converted into vapor, the molecules have to overcome the atmospheric pressure or other external resistance, and, in consequence of this, together with the internal work already spoken of, a large quantity of heat disappears, or is rendered *latent*, the quantity thus consumed being, to a considerable extent, affected by the external pressure. The liquefaction of a solid not being attended with much increase of volume, involves but little external work; nevertheless the atmospheric pressure does influence, to a slight amount, both the latent heat of fusion and the melting-point.

LIGHT.

TWO views have been entertained respecting the nature of light. Sir Isaac Newton imagined that luminous bodies emit, or shoot out, infinitely small particles in straight lines, which, by penetrating the transparent parts of the eye and falling upon the nervous tissue, produce vision. Other philosophers drew a parallel between the properties of light and those of sound, and considered that, as sound is certainly the effect of undulations, or little waves, propagated through elastic bodies in all directions, so light might be nothing more than the consequence of similar undulations transmitted with inconceivable velocity through a highly elastic medium, of excessive tenuity, filling all space, and occupying the intervals between the particles of material substances. To this medium they gave the name of *ether*. The wave hypothesis of light is at present generally adopted. It is in harmony with all the known phenomena discovered since the time of Newton, not a few of which were first deduced from the undulatory theory, and afterwards verified by experiment. Several well-known facts are in direct opposition to the theory of emission.

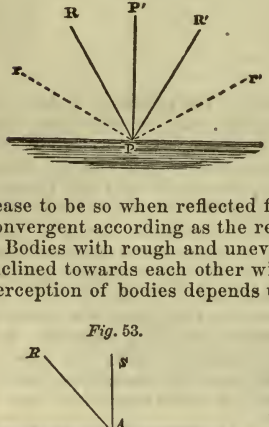
A ray of light emitted from a luminous body proceeds in a straight line, and with extreme velocity. Certain astronomical observations afford the means of approximating to a knowledge of this velocity. The satellites of Jupiter revolve about the planet in the same manner as the moon about the earth, and the time required by each satellite for the purpose is exactly known from its periodical entry into or exit from the shadow of the planet. The time required by one is only 42 hours. Römer, the astronomer of Copenhagen, found that this period appeared to be longer when the earth, in its passage round the sun, moved from the planet Jupiter; and, on the contrary, he observed that the periodic time appeared to be shorter when the earth moved in the direction towards Jupiter. The difference, though very small for a single revolution of the satellite, increases, by the addition of many revolutions, during the passage of the earth from its nearest to its greatest distance from Jupiter, that is, in about half a year, till it amounts to 16 minutes and 16 seconds. Römer concluded from this, that the light of the sun, reflected from the satellite, required that time to pass through a distance equal to the diameter of the orbit of the earth; and since this place is little short of 200 millions of miles, the velocity of light cannot be less than 200,000 miles in a second of time. It will be seen hereafter that this rapidity of transmission is rivalled by that of electricity. Another astronomical phenomenon, observed and correctly explained by Bradley, the aberration of the fixed stars, leads to the same result. Physicists have, moreover, succeeded in measuring the velocity of light for terrestrial, and, indeed, comparatively small distances; the results of these experiments essentially correspond with those given by astronomical observations.

When a ray of light falls upon a boundary between two media, a part of it, and, in exceptional cases, the whole, is reflected into the first medium, whilst the other part penetrates the second medium.

The law of regular reflection is extremely simple. If a line be drawn perpendicular to the surface upon which the ray falls, and the angle contained between the ray and the perpendicular measured, it will be found

that the ray, after reflection, takes such a course as to make with the perpendicular an equal angle on the opposite side of the latter. A ray of light, R, falling at the point P, will be reflected in the direction PR′, making the angle R′PP′ equal to the angle RPP′; and a ray from the point *r* falling upon the same spot will be reflected to *r′* in virtue of the same law. Further, it is to be observed that the incident and reflected rays are always contained in the same normal plane.

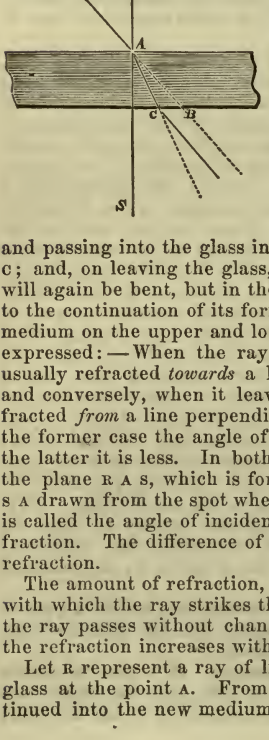
Fig. 52.



The same rule holds good if the mirror be curved, as a portion of a sphere, the curve being considered as made up of a multitude of little planes. Parallel rays cease to be so when reflected from curved surfaces, becoming divergent or convergent according as the reflecting surface is convex or concave.

Bodies with rough and uneven surfaces, the smallest parts of which are inclined towards each other without order, reflect the light diffused. The perception of bodies depends upon the diffused reflected light.

Fig. 53.



It has just been stated that light passes in straight lines; but this is true only so long as the medium through which it travels preserves the same density and the same chemical nature: when this ceases to be the case, the ray of light is bent from its course into a new one, or is said to be *refracted.*

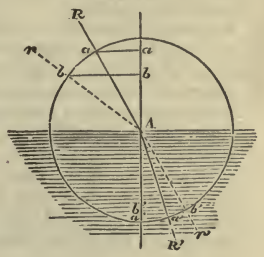
Let R be a ray of light falling upon a plate of some transparent substance with parallel sides, such as a piece of thick plate glass, — in short, any transparent homogeneous material which is either non-crystalline, or crystallizes in the regular system; and let A be its point of contact with the upper surface. The ray, instead of holding a straight course and passing into the glass in the direction A B, will be bent downwards to C; and, on leaving the glass, and issuing into the air on the other side, it will again be bent, but in the opposite direction, so as to make it parallel to the continuation of its former track, provided there be one and the same medium on the upper and lower side of the plate. The general law is thus expressed: — When the ray passes from a rare to a denser medium, it is usually refracted *towards* a line perpendicular to the surface of the latter; and conversely, when it leaves a dense medium for a rarer one, it is refracted *from* a line perpendicular to the surface of the denser substance; in the former case the angle of incidence is greater than that of refraction; in the latter it is less. In both cases the direction of the refracted ray is in the plane R A S, which is formed by the falling ray and the perpendicular S A drawn from the spot where the ray is refracted; the angle R A S = B A S′, is called the angle of incidence. The angle C A S′ is called the angle of refraction. The difference of these two angles, that is, the angle C A B, is the refraction.

The amount of refraction, for the same medium, varies with the obliquity with which the ray strikes the surface. When perpendicular to the latter, the ray passes without change of direction at all; and in other positions, the refraction increases with the obliquity.

Let R represent a ray of light falling upon the surface of a mass of plate glass at the point A. From this point let a perpendicular fall and be continued into the new medium; and around the same point, as a centre, let

a circle be drawn. According to the law just stated, the refraction must be towards the perpendicular; in the direction A R′, for example. Let the lines *a*—*a*, *a′*—*a′*, at right angles to the perpendicular, be drawn, and their length compared by means of a scale of equal parts, and noted; their length will in the case supposed be in the proportion of 3 to 2. These lines are termed the *sines* of the angles of incidence and refraction respectively.

Fig. 54.



Now let another ray be taken, such as *r;* it is refracted in the same manner to *r′*, the bending being greater from the increased obliquity of the ray; but what is very remarkable, if the sines of the two new angles of incidence and refraction be again compared, they will still be found to bear to each other the proportion of 3 to 2. The fact is expressed by saying, that so long as the light passes from one to the other of the same two media, the *ratio of the sines of the angles of incidence and refraction is constant.* This ratio is called the *index of refraction.*

Different bodies possess different refractive powers; generally speaking, the densest substances refract most. Combustible bodies have been noticed to possess greater refractive power than their density would indicate, and from this observation Sir I. Newton predicted the combustible nature of the diamond long before anything was known respecting its chemical nature.

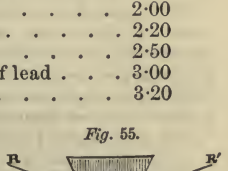
The method adopted for describing the comparative refractive power of different bodies, is to state the ratio borne by the sine of the angle of incidence in the first medium, and on the boundary of the second, to the sine of the angle of refraction in this second medium; this is called the *index of refraction* of the two substances; it is greater or less than unity, according as the second medium is denser or rarer than the first. In the case of air and plate glass the index of refraction is 1·5.

When the index of refraction of any particular substance is once known, the effect of the latter upon a ray of light entering it in any position can be calculated by the law of sines. The following table exhibits the indices of refraction of several substances, supposing the ray to pass into them from the air: —

Substances.	Index of refraction.	Substances.	Index of refraction.
Tabasheer* . . .	1·10	Garnet	1·80
Ice	1·30	Glass, with much oxide of lead	1·90
Water	1·34	Zircon	2·00
Fluor spar.	1·40	Phosphorus.	2·20
Plate glass	1·50	Diamond	2·50
Rock-crystal	1·60	Chromate of lead . . .	3·00
Chrysolite	1·69	Cinnabar	3·20
Bisulphide of carbon .	1·70		

When a luminous ray enters a mass of substance differing in refractive power from the air, and whose surfaces are not parallel, it becomes permanently deflected from its course and altered in its direction. It is upon this principle that the properties of prisms and lenses depend. To take an example. — Fig. 55 represents a triangular prism of glass, upon the side of which the ray of light R may be supposed to fall. This ray will

Fig. 55.



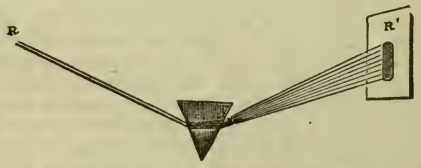
* A siliceous deposit in the joints of the bamboo.

of course be refracted, on entering the glass, towards a line perpendicular to the first surface, and again, from a line perpendicular to the second surface on emerging into the air. The result is the deflecton *a c* R, which is equal to the sum of the two deflections which the ray undergoes in passing through the prism.

A convex lens is thus enabled to converge rays of light falling upon it, and a concave lense to separate them more widely; each separate part of the surface of the lens producing its own independent effect.

The light of the sun and celestial bodies in general, as well as that of the electric spark and of all ordinary flames, is of a compound nature. If a ray of light from any of the sources mentioned be admitted into a dark room by a small hole in a shutter, or otherwise, and suffered to fall upon a glass prism in the manner shown in fig. 56, it will not only be refracted from its straight course, but will be decomposed into a number of colored rays, which may be received upon a white screen placed behind the prism. When solar light is employed, the colors are extremely brilliant, and spread into

Fig. 56.



an oblong space of considerable length. The upper part of this image, or *spectrum*, will be violet and the lower red, the intermediate portion, commencing from the violet, being indigo, blue, green, yellow, and orange, all graduating imperceptibly into each other. This is the celebrated experiment of Sir Isaac Newton; from it he drew the inference that white light is composed of seven primitive colors, the rays of which are differently refrangible by the same medium, and hence capable of being thus separated. The violet rays are most refrangible, and the red rays least.*

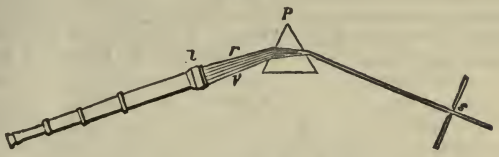
Bodies of the same mean refractive power do not always equally disperse or spread out the differently colored rays to the same extent; because the principal yellow or red rays, for instance, are equally refracted by two prisms of different materials, it does not follow that the blue or the violet will be similarly affected. Hence, prisms of different varieties of glass, or other transparent substances, give, under similar circumstances, very different spectra, both as respects the length of the image, and the relative extent of the colored bands.

The appearance of the spectrum may also vary with the nature of the source of light: the investigation of these differences, however, involves the use of a more delicate apparatus. Fig. 57 shows the principle of such an apparatus, which is called a *spectroscope*. The light, passing through a fine slit, *s*, impinges upon a flint-glass prism, *p*, by which it is dispersed. The decomposed light emerges from the prism in several directions between *r* (red rays) and *v* (violet rays); and the spectrum thus produced is observed

* The colors of natural objects are supposed to result from the power possessed by their surfaces of absorbing some of the colored rays, while they reflect or transmit, as the case may be, the remainder of the rays. Thus an object appears red because it absorbs or causes to disappear the yellow and blue rays composing the white light by which it is illuminated. Any color which remains after the deduction of another color from white light, is said to be *complementary* to the latter. Complementary colors, when acting simultaneously, reproduce white light. Thus in the example already quoted, red and green — the latter resulting from yellow and blue — are complementary colors. The fact of complementary colors giving rise to white light may be readily illustrated by mixing in appropriate quantities a rose-red solution of cobalt and green solution of nickel; the resulting liquid is nearly colorless.

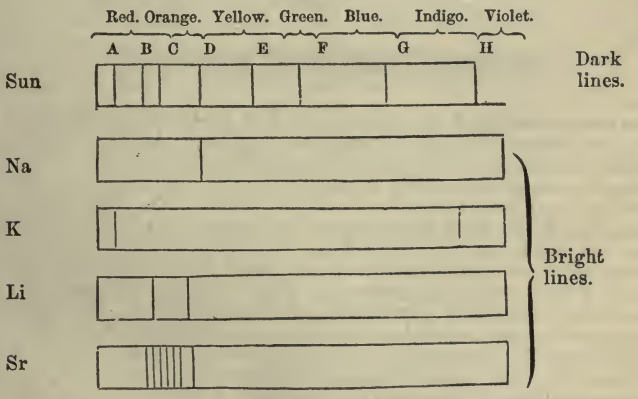
by the telescope *t*, which receives only part of it at once; but the several parts may be readily examined by turning slightly either the prism, *p*, or the telescope, *t*.

Fig. 57.



If the solar spectrum be examined in this manner, numerous dark lines parallel with the edge of the prism are observed. They were discovered in 1802 by Dr. Wollaston, and subsequently more minutely investigated by Fraunhofer. They are generally known as Fraunhofer's lines. These dark lines, which exist in great numbers, and of very varying strength, are irregularly distributed over the whole spectrum. Some of them, in consequence of their peculiar strength and their mutual position, may always be easily recognized; the more conspicuous are represented in fig. 58. The same dark lines, though paler, and much more difficult to recognize, are

Fig. 58.



observed in the spectrum of planets lighted by the sun; for instance, in the light emanating from Venus. On the other hand, the dark lines observed in the spectra, which are produced by the light emanating from fixed stars — from Sirius, for instance — differ in position from those previously mentioned.

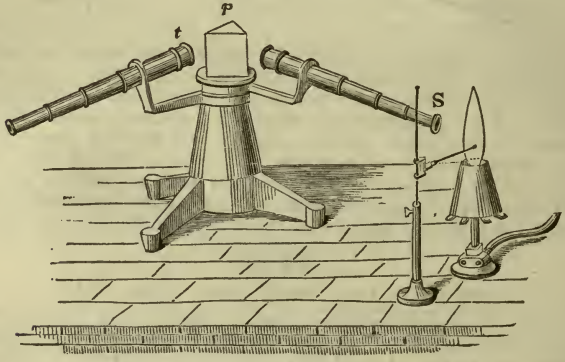
Sources of light which contain no volatile constituents — incandescent platinum wire, for example — furnish continuous spectra, exhibiting no such lines. But if volatile substances be present in the source of light, bright lines are observed in the spectrum, which are frequently characteristic of the volatile substances.

Professor Plücker, of Bonn, has investigated the spectra which are produced by the electric light when developed in very rarefied gases. He found the bright lines and the dark stripes between the lines varying considerably with different gases. When the electric light was developed in a

mixture of two gases, the spectrum thus obtained exhibited simultaneously the peculiar spectra belonging to the two gases of which the mixture consisted. When the experiment was made in gaseous compounds capable of being decomposed by the electrical current, this decomposition was indicated by the spectra of the separated constituents becoming perceptible.

Many years ago the spectra of colored flames were examined by Sir John Herschel, Fox Talbot, and W. A. Miller. Within the last few years results of the greatest importance have been obtained by Kirchhoff and Bunsen,

Fig. 59.



who have investigated the spectra furnished by the incandescence of volatile substances: these researches have enriched chemistry with a new method of analysis,—the analysis by spectrum observations. In order to recognize one of the metals of the alkalies or of the alkaline earths, it is generally sufficient to introduce a minute quantity of a moderately volatile compound of the metal on the loop of a platinum wire into the edge of the very hot, but scarcely luminous flame, of a mixture of air and coal-gas, and to examine the spectrum which is furnished by the flame containing the vapor of the metal or its compound. Fig. 59 exhibits the apparatus which is used in performing experiments of this description. The light of the flame in which the metallic compound is evaporated passes through the fine slit in the disc, *s*, into a tube, the opposite end of which is provided with a convex lens. This lens collects the rays diverging from the slit, and throws them parallel upon the prism, *p*. The light is decomposed by the prism, and the spectrum thus obtained is observed by means of the telescope, which may be turned round the axis of the stand carrying the prism. Foreign light is excluded by an appropriate covering.

The limits of this elementary treatise do not permit us to describe the ingenious arrangements which have been contrived for sending the light from different sources through the same prism at different heights, whereby their spectra, the solar spectrum, for instance, and that of a flame, may be placed in a parallel position, the one above the other, and thus be compared.* The spectra of flames in which different substances are volatilized frequently exhibit such characteristically distinct phenomena, that they may be used with the greatest advantage for the discrimination of these substances. Thus the spectrum of a flame containing sodium (Na) exhibits a bright line on

* See the article "Spectral Analysis," by Prof. Roscoe, in Watts's Dictionary of Chemistry, vol. i.

the yellow portion, the spectrum of potassium (K) a characteristic bright line at the extreme limit of the red, and another at the opposite violet limit of the spectrum. Lithium (Li) shows a bright brilliant line in the red, and a paler line in the yellow portion; strontium (Sr) a bright line in the blue, one in the orange, and six less distinct ones in the red portion of the spectrum. The diagram (fig. 58) exhibits the most remarkable of the dark lines (Fraunhofer's lines), and the position of the bright lines in the spectra of flames containing the vapors of compounds of the several metals enumerated.

The delicacy of these spectral reactions is very considerable, but unequal in the case of different metals. The presence of $\frac{1}{200,000,000}$ grain of sodium in the flame is still easily recognizable by the bright yellow line in the spectrum. Lithium, when introduced in the form of a volatile compound, imparts to the flame a red color; but this coloration is no longer perceptible when a volatile sodium compound is simultaneously present, the yellow coloration of the flame predominating under such circumstances. On the other hand, when a mixture of one part of lithium and 1000 parts of sodium is volatilized in a flame, the spectrum of the flame exhibits, together with the bright yellow sodium line, likewise the red line characteristic of lithium. The observation of bright lines not belonging to any of the previously known bodies has led to the discovery of new elements. Thus, Bunsen and Kirchhoff, when examining the spectrum of a flame in which a mixture of alkaline salt was evaporated, observed some bright lines, which could not be attributed to any of the known elements, and were thus led to the discovery of the two new metals, cæsium and rubidium. By the same method a new element, thallium, has been more recently discovered by Mr. Crookes.

For the examination of the bright lines in the spectra of metals, the electric spark, passing between two points of the metal under examination, may be conveniently employed as a source of light. Small quantities of the metal are invariably volatilized; and the spectrum developed by the electric light exhibits the bright lines characteristic of the metal employed. These lines were observed by Wheatstone as early as 1835. This method of investigation is more especially applicable to the examination of the spectra of the heavy metals.

By a series of theoretical considerations, Professor Kirchhoff has arrived at the conclusion that the spectrum of an incandescent gas is reversed—*i. e.*, that the bright lines become dark lines, if there be behind the incandescent gas a very luminous source of light, which by itself furnishes a continuous spectrum. Kirchhoff and Bunsen have fully confirmed this conclusion by experiment. Thus a volatile lithium salt produces, as just pointed out, a very distinct bright line in the red portion of the spectrum; but if bright sunlight, or the light emitted by a solid body heated to the most powerful incandescence, be allowed to fall through the flame upon the prism, the spectrum exhibits, in the place of this bright line, a black line similar in every respect to Fraunhofer's lines in the solar spectrum. In like manner the bright strontium line is reversed into a dark line. Kirchhoff and Bunsen have expressed the opinion that all the Fraunhofer lines in the solar spectrum are bright lines thus reversed. In their conception, the sun is surrounded by a luminous atmosphere, containing a certain number of volatilized substances, which would give rise in the spectrum to certain bright lines, if the light of the solar atmosphere alone could reach the prism; but the intense light of the powerful incandescent body of the sun which passes through the solar atmosphere, causes these bright lines to be reversed, and to appear as dark lines on the ordinary solar spectrum. Kirchhoff and Bunsen have thus been enabled to attempt the investigation of the chemical constituents of the solar atmosphere, by ascertaining the elements which,

when in the state of incandescent vapor, develop bright spectral lines, coinciding with Fraunhofer's lines in the solar spectrum. Fraunhofer's line D (fig. 58) coincides most accurately with the bright spectral line of sodium, and may be artificially produced by reversing the latter; sodium would thus appear to be a constituent of the solar atmosphere. Kirchhoff has proved, moreover, that sixty bright lines perceptible in the spectrum of iron correspond, both as to position and distinction, most exactly with the same number of dark lines in the solar spectrum; and, accordingly, he believes iron, in the state of vapor, to be present in the solar atmosphere. In a similar manner this physicist has endeavored to establish the presence of several other elements in the solar atmosphere.

Absorption Spectra. — The relative quantities of the several colored rays absorbed by a colored medium of given thickness may be observed by viewing a line of light through a prism and the colored medium; the spectrum will then be seen to be diminished in brightness in some parts, and perhaps cut off altogether in others. This mode of observation is often of great use in chemical analysis, as many colored substances when thus examined afford very characteristic spectra, the peculiarities of which may often be distinguished, even though the solution of the substance under examination contains a sufficient amount of colored impurities to change its color very considerably. The following method of making the observation is given by Professor Stokes.*

A small prism is to be chosen of dense flint glass, ground to an angle of 60°, and just large enough to cover the eye comfortably. The top and bottom should be flat, for convenience of holding the prism between the thumb and fore-finger, and laying it down on a table, so as not to scratch or soil the faces. A fine line of light is obtained by making a vertical slit in a board six inches square, or a little longer in a horizontal direction, and adapting to the aperture two pieces of thin metal. One of the metal pieces is movable, to allow of altering the breadth of the slit. About the fiftieth of an inch is a suitable breadth for ordinary purposes. The board and metal pieces should be well blackened.

On holding the board at arm's length against the sky or a luminous flame, the slit being, we will suppose, in a vertical direction, and viewing the line of light thus formed through the prism held close to the eye, with its edge vertical, a pure spectrum is obtained at a proper azimuth of the prism. Turning the prism round its axis alters the focus, and the proper focus is got by trial. The whole of the spectrum is not, indeed, in perfect focus at once, so that in scrutinizing one part after another it is requisite to turn the prism a little. When daylight is used, the spectrum is known to be pure by its showing the principal fixed lines; in other cases the focus is got by the condition of seeing distinctly the other objects, whatever they may be, which are presented in the spectrum. To observe the absorption-spectrum of a liquid, an elastic band is put round the board near the top, and a test-tube containing the liquid is slipped under the band, which holds it in its place behind the slit. The spectrum is then observed just as before, the test-tube being turned from the eye.

To observe the whole progress of the absorption, different degrees of strength must be used in succession, beginning with a strength which does not render any part of the spectrum absolutely black, unless it be one or more very narrow bands, as otherwise the most distinctive features of the absorption might be missed. If the solution be contained in a wedge-shaped vessel instead of a test-tube, the progress of the absorption may be watched in a continuous manner by sliding the vessel before the eye. Some observers prefer using a wedge-shaped vessel in combination with the slit,

* Chem. Soc. Journ. xvii. 306.

the slit being perpendicular to the edge of the wedge. In this case each element of the slit forms an elementary spectrum corresponding to a thickness of the solution which increases in a continuous manner from the edge of the wedge, where it vanishes. This is the mode of observation adopted by Gladstone.*

Fig. 60 represents the effect produced in this way by a solution of chromic chloride, and fig. 61 that produced by a solution of potassium permanganate.

Fig. 60.

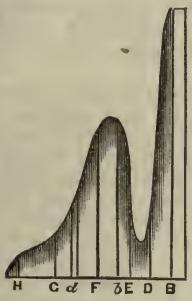
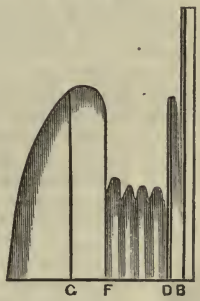


Fig. 61.



The right-hand side of these figures corresponds with the red end of the spectrum; the letters refer to Fraunhofer's lines. The lower part of each figure shows the pure spectrum seen through the thinnest part of the wedge; and the progress of the absorption, as the thickness of the liquid increases, is seen by the gradual obliteration of the spectrum towards the upper part of the figures.

Fluorescence. — An examination into a peculiar mode of analysis of light, discovered by Sir John Herschel, in a solution of quinine sulphate, has within the last few years led to the discovery of a most remarkable fact. Mr. Stokes has observed that light of certain refrangibility and color is capable of experiencing a peculiar influence in being dispersed by certain media, and of undergoing thereby an alteration of its refrangibility and color. This curious change, called fluorescence, can be produced by a great number of bodies, both liquid and solid, transparent and opaque. Frequently the change affects only the extreme limits; at other times larger portions, and in a few cases even the whole, or, at all events, the major part of the spectrum. A dilute solution of quinine sulphate, for instance, changes the violet and the dark-blue light to sky-blue; by a decoction of madder in a solution of alum all rays of higher refrangibility than yellow are converted into yellow; by an alcoholic solution of the coloring matter of leaves all the rays of the spectrum become red. In all cases in which this peculiar phenomenon presented itself in a greater or less degree, Mr. Stokes observed that it consisted in a diminution of the refrangibility. Thus, rays of so high a degree of refrangibility, that they extend far beyond the extreme limits of the spectrum visible under ordinary circumstances, may be rendered luminous, and converted into blue and even red light.

Double Refraction and Polarization. — A ray of common light made to pass through certain crystals of a particular order is found to undergo a very remarkable change. It becomes split or divided into two rays, one of

* Chem. Soc. Journ. x. 79.

which follows the general law of refraction, while the other takes a new and extraordinary course, dependent on the position of the crystal. This effect, which is called *double refraction*, is beautifully illustrated in the case of Iceland spar, or crystallized calcium carbonate. On placing a rhomb of this substance on a piece of white paper on which a mark or line has been made, the object will be seen double.

Again, if a ray of light be suffered to fall on a plate of glass at an angle of 56° 45′, the portion of the ray which suffers reflection will be found to have acquired properties which it did not before possess; for on throwing it, at the same angle, upon a second glass plate, it will be observed that there are two particular positions of the latter, namely, those in which the planes of incidents are at right angles to one another, when the ray of light is no longer reflected, but entirely refracted. Light which has suffered this change is said to be *polarized*.

The light which passes through the first or polarizing plate is, also, to a certain extent, in this peculiar condition, and by employing a series of similar plates held parallel to the first, this effect may be greatly increased; a bundle of fifteen or twenty such plates may be used with great convenience for the experiment. It is to be remarked, also, that the light polarized by transmission in this manner is in an opposite state to that polarized by reflection; that is, when examined by a second or *analyzing* plate, held at the angle before mentioned, it will be seen to be reflected when the other is transmitted, and to be dispersed when the first is reflected.

Fig. 62.

It is not every substance which is capable of polarizing light in this manner; glass, water, and certain other bodies bring about the change in question, each having a particular polarizing angle at which the effect is greatest. The metals also can, by reflection, polarize the light, but they do so very imperfectly. The two rays into which a pencil of common light divides itself in passing through a doubly refracting crystal are found on examination to be polarized in a very complete manner, and also transversely, the one being capable of reflection when the other vanishes or is transmitted. The two rays are said to be polarized in opposite directions. With a rhomb of transparent Iceland spar of tolerably large dimensions, the two oppositely polarized rays may be widely separated and examined apart.

Certain doubly refracting crystals absorb the one of these rays, but not the other. Through a plate of such a crystal one ray passes and becomes entirely polarized; the other, which is likewise polarized, but in another plane, is removed by absorption. The best known of these media is tourmaline. When two plates of this mineral, cut parallel to the axis of the crystal, are held with their axes parallel, as in fig. 63, light traverses them both freely; but when one of them is turned round in the manner shown in fig. 64, so as to make the axes cross at right angles, the light is almost

Fig. 63

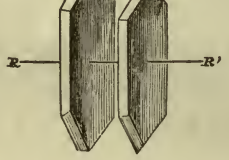
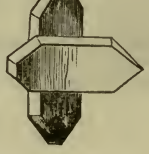


Fig. 64.



wholly stopped, if the tourmalines are good. A plate of the mineral thus becomes an excellent test for discriminating between polarized light and that which has not undergone the change.

Some of the most splendid phenomena of the science of light are exhibited when thin plates of doubly refracting substances are interposed between the polarizing arrangement and the analyzer.

Instead of the tourmaline plate, which is always colored, frequent use is made of two Nichol's prisms, or conjoined prisms of calcium carbonate, which, in consequence of a peculiar cutting and combination, possess the property of allowing only one of the oppositely polarized rays to pass. A more advantageous method of cutting and combining prisms has been given by M. Foucault. His prisms are as serviceable as and less expensive than those of Nichol. If two Nichol's or Foucault's prisms be placed one behind the other in precisely similar positions, the light polarized by the one goes through the other unaltered. But when one prism is slightly turned round in its setting, a cloudiness is produced; and by continuing to turn the prism, this increases until perfect darkness ensues. This happens, as with the tourmaline plates, when the two prisms cross one another. The phenomenon is the same with colorless as with colored light.

Circular Polarization.—Supposing that polarized light, colored, for example, by going through a plate of red glass, has passed through the first Nichol's prism, and been altogether obstructed in consequence of the position of the second prism, then, if between the two prisms a plate of rock-crystal formed by a section at right angles to the principal axis of the crystal, be interposed, the light polarized by the first prism will, by passing through the plate of quartz, be enabled partially to pass through the second Nichol's prism. Its passage through the second prism can then again be interrupted by turning the second prism round to a certain extent. The rotation required varies with the thickness of the plate of rock-crystal, and also with the color of the light employed. It increases from red in the following order — yellow, green, blue, violet.

This property of rock-crystal was discovered by Arago. The kind of polarization has been called circular polarization. The direction of the rotation is with many plates towards the right hand; in other plates it is towards the left. The one class is said to possess right-handed polarization, the other class left-handed polarization. For a long time quartz was the only solid body known to exhibit circular polarization. Others have since been found which possess this property in a far higher degree. Thus, a plate of cinnabar acts fifteen times more powerfully than a plate of quartz of equal thickness.

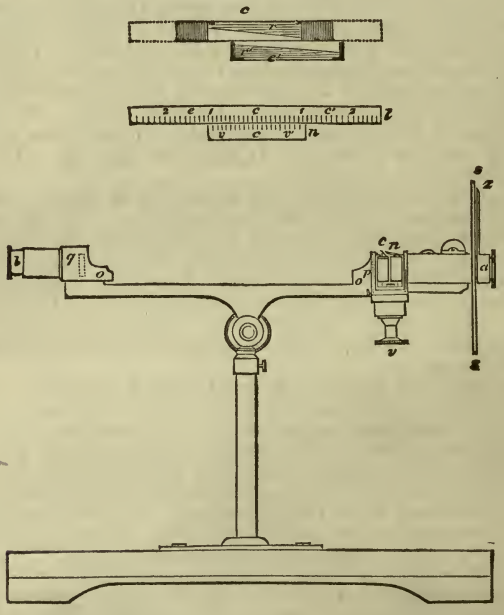
Biot observed that many solutions of organic substances exhibit the property of circular polarization, though to a far less extent than rock-crystal. Thus, solutions of cane-sugar, glucose, and tartaric acid, possess right-handed polarization; whilst albumen, uncrystallizable sugar, and oil of turpentine, are left-handed. In all these solutions the amount of circular polarization increases with the concentration of the liquid and the thickness of the column through which the light passes. Hence circular polarization is an important auxiliary in chemical analysis. In order to determine the amount of polarization which any liquid exhibits, it is put into a glass tube not less than from ten to twelve inches long, which is closed with glass plates. This is then placed between the two Nichol's prisms, which have previously been so arranged with regard to each other that no light could pass through. An apparatus of this description, the saccharimeter, is used for determining the concentration of solutions of cane-sugar.

The form of this instrument may be seen in fig. 65. The two Nichol's prisms are enclosed in the corresponding fastenings *a* and *b*. Between the two there is a space to receive the tube, which is filled with the solution of

sugar. If the prisms are crossed in the way above mentioned before the tube is put in its place, that is, if they are placed so that no light passes them, then by the action of the solution of sugar the light is enabled to pass, and the Nichol's prism, *a*, must be turned through a certain angle before the light is again perfectly stopped. The magnitude of this angle is observed on the circular disk *s s*, which is divided into degrees, and upon which, by the turning of the prism, an index *z* is moved along the division. When the tube is exactly ten inches long, and is closed at both ends by flat glass plates, and when it is filled with solution containing 10 per cent. by weight of cane-sugar, and free from any other substance possessing an action on light, the angle of rotation is 13·35°. Since the magnitude of this angle stands in direct relation to the length of the column of liquid and also to the quantity of sugar in solution, it is clear that the quantity of sugar in any given solution, when the length of the column of liquid is *l* inches, and the angle of rotation is *a* degrees, can be determined by the equation $z = \frac{a \times l}{13{\cdot}35}$.

This process is not sufficient when the solution contains cane-sugar and uncrystallizable sugar: for the latter rotates the ray to the left; in that

Fig. 65.



case only the difference of the two actions is obtained. But if the whole quantity of sugar be changed into uncrystallizable sugar, and the experiment be repeated, then from the results of the two observations the quantity of both kinds of sugar can easily be calculated.

It is difficult to find exactly that position of the Nichol's prisms in which

the greatest darkness prevails. To make the measurements more exact and easy, Soleil has made some additions to the apparatus. At *q*, before the prism *b*, a plate of rock-crystal cut at right angles to the axis is placed. It is divided in the centre of the field of vision, half consisting of quartz rotating to the right hand, and half of the variety which rotates to the left; it is 0·148 inch (3·75 millimetre) thick, this thickness being found by experiment to produce the greatest difference in the color of the two halves, when one prism is slightly rotated. The solution of sugar has precisely the same action on the rotation, since it increases the action of the half which has a right-handed rotation, and lessens the action of the half which rotates to the left. Hence the two halves will assume a different color when the smallest quantity of sugar is present in the liquid. By slightly turning the Nichol's prism *a*, this difference can be again removed. Soleil has introduced another more delicate means of effecting this at the part *p*, which he calls the compensator. The most important parts of this are separately represented in fig. 65. It consists of two exactly equal right-angled prisms, of left-handed quartz, whose surfaces, *c'* and *c*, are cut perpendicular to the optic axis. These prisms can, by means of the screw *v* and a rack and pinion, be made to slide on one another, so that, when taken together, they form a plate of varying thickness, bounded by parallel surfaces. One of the frames has a scale *p*, the other a vernier *n*. When this points to zero of the scale, the optical action of the two prisms is exactly compensated by a right-handed plate of rock-crystal, so that an effect is obtained as regards circular polarization, as if the whole system were not present. As soon, however, as the screw is moved, and thus the thickness of the plate formed by the two prisms is changed (we will suppose it increased), then a left-handed action ensues, which must be properly regulated, until it compensates the opposite action of a solution of sugar. Thus a convenient method is obtained of rendering the color of the double plate uniform, when it has ceased to be so by the action of the sugar.

Faraday has made the remarkable discovery that, if a very strong electric current be passed round a substance which possesses the property of circular polarization, the amount of rotation is altered to a considerable degree.

Heating and Chemical Rays of the Solar Spectrum. — The luminous rays of the sun are accompanied, as already mentioned, by others which possess heating powers. If the temperature of the different-colored spaces in the spectrum be tried with a delicate thermometer, it will be found to increase from the violet to the red extremity, and when the prism is of some particular kinds of glass, the greatest effect will be manifested a little beyond the visible red rays. The position of the greatest heating effect in the spectrum materially depends on the absorptive nature of the glass. Transparent though this medium is to the rays of light, it nevertheless absorbs a considerable quantity of the heat rays. Transparent rock-salt is almost without absorptive action on the thermal rays. In the spectrum obtained by passing the solar rays through prisms of rock-salt, the greatest thermal effect is found at a position far beyond the last visible red rays. It is inferred from this that the chief mass of the heating rays of the sun are among the least refrangible components of the solar beam.

Again, it has long been known that chemical changes both of combination and of decomposition, but more particularly the latter, can be effected by the action of light. Chlorine and hydrogen combine at common temperatures only under the influence of light; and parallel cases occur in great numbers in organic chemistry. The blackening and decomposition of silver salts are familiar instances of the chemical powers of the same agent. Now, it is not always the luminous part of the ray which effects these changes;

they are chiefly produced by certain invisible rays, which accompany the others, and are found most abundantly beyond the violet part of the spectrum. It is there that certain chemical effects are most marked, although the intensity of the light is exceedingly feeble. From the fact that some salts of silver are less readily decomposed by the luminous — yellow, orange, and red rays — than by certain rays which extend beyond the ordinary visible spectrum, it has been concluded that there exists in the sunbeam, in addition to heat and light, a principle having a distinct action, to which the provisional term *actinism* has been given — from ἀκτίς, a ray. The actinic rays are thus directly opposed to the heating rays in the common spectrum in their degree of refrangibility, since they exceed all the others in this respect. The luminous rays, too, under peculiar conditions, exert decomposing powers upon silver salts. The result of the action of any ray depends, moreover, greatly on the physical state of the surface upon which it falls, and on the chemical constitution of the body; indeed, for every kind of ray a substance may be found which under particular circumstances will be affected by it; and thus it appears that the chemical functions are by no means confined to any set of rays to the exclusion of the rest.

Upon the chemical changes produced by light is based the art of *photography*. In the year 1802, Mr. Thomas Wedgwood proposed a method of copying paintings on glass by placing behind them white paper or leather moistened with a solution of silver nitrate, which became decomposed and blackened by the transmitted light in proportion to the intensity of the latter; and Davy, in repeating these experiments, found that he could thus obtain tolerably accurate representations of objects of a texture partly opaque and partly transparent, such as leaves and the wings of insects, and even copy with a certain degree of success the images of small objects obtained by the solar microscope. These pictures, however, required to be kept in the dark, and could only be examined by candle-light, otherwise they became obliterated by the blackening of the whole surface from which the salt of silver could not be removed These attempts at light-painting attracted but little notice till the publication of Mr. Fox Talbot's papers, read before the Royal Society, in January and February, 1839, in which he detailed two methods of fixing the pictures produced by the action of light on paper impregnated with silver chloride, and at the same time described a plan by which the sensibility of the prepared paper may be increased to the extent required for receiving impressions from the images of the camera obscura.

Very shortly afterwards, Sir John Herschel proposed to employ solutions of the alkaline hyposulphites for removing the excess of silver chloride from the paper, and thus preventing the further action of light; and this plan has been found exceedingly successful. The greatest improvement, however, which the curious art of photogenic drawing has received, is due to Mr. Talbot, who, in a communication to the Royal Society, described a method by which paper of such sensibility could be prepared as to permit its application to the taking of portraits of living persons by the aid of a good camera obscura, the time required for a perfect impression seldom exceeding a few seconds. The plan at present in use is the following:

Writing-paper of good quality is washed on one side with a solution of thirty grains of silver nitrate in one ounce of distilled water, and then left to dry spontaneously in a dark room; when dry, it is immersed for from five to ten minutes in a solution of one ounce of potassium iodide in twenty ounces of water. The paper is then soaked in water for half an hour, changing the water three or four times to remove the excess of potassium iodide, and is then dried. These operations should be performed by candle-light. When required for use, the paper, thus coated with yellow silver

iodide, is brushed over with a solution made by adding together one part of a solution of silver nitrate, fifty grains to one ounce of water; two parts glacial acetic acid, and three parts of a saturated solution of gallic acid; after a few seconds the excess is removed by blotting-paper. This, which is called *Talbotype* or *Calotype* paper, is now ready for use; exposure to diffused daylight for one second suffices to make an impression upon it, and even the light of the moon produces the same effect, although a much longer time is required. For landscapes and fixed objects, and when the paper is required to be prepared long beforehand, the above mixture of "*gallo-nitrate*" should be diluted with from twenty to fifty volumes of water, since, especially in hot weather, without this precaution the paper blackens spontaneously.

The images of the camera obscura are at first invisible, but are made to appear in full intensity, by once more washing the paper with a mixture of one part of the silver solution (fifty grains to an ounce of water) and four parts of the saturated solution of gallic acid. The image soon appears, and should be fully developed in a few minutes.

The picture is of course *negative*, the lights and shadows being reversed; to obtain *positive* copies, nothing more is necessary than to place a piece of photographic paper prepared with silver chloride, or a piece of talbotype paper, beneath the negative cover, to press the two papers in contact by means of a glass, and to expose the whole to the light of the sun for a short time, or longer to diffused daylight.

Before this can be done, the negative must, however, be fixed, otherwise it will blacken: this is done temporarily by washing with a solution of potassium bromide, ten grains in an ounce of water, and then rinsing in common water. The ultimate fixing is effected by immersion in a solution of one part of sodium hyposulphite, in from four to ten parts of water: the weaker solution should be used hot, about 82° C. (180° F.), and the immersion continued until the yellow tint arising from the undecomposed iodide disappears: finally, *repeatedly washing* in hot water, drying, and saturating with white wax, terminates the process.

The positives are also fixed by sodium hyposulphite, by potassium cyanide, or by ammonia; all of which act by removing the undecomposed silver chloride. The conservation of the positive is a point of difficulty. Mr. Malone recommends immersion in a strong solution of caustic potassa, heated to about 82° C.; a change of tint ensues, and greater permanence is acquired. After removal of the alkali and any sulphur and chlorine compounds present, the picture should be sized and hot-pressed, or varnished, keeping the finished proof most carefully excluded from sulphuretted vapors.

Sir John Herschel has shown that a great number of other substances can be employed in these photographic processes by taking advantage of the singular deoxidizing effects of certain portions of the solar rays. Paper washed with a solution of ferric salt becomes capable of receiving impressions of this kind, which may afterwards be made evident by potassium ferricyanide, or gold chloride. Vegetable colors are also acted upon in a very curious and apparently definite manner by the different parts of the spectrum.

The daguerreotype, the announcement of which was first made in the summer of 1839, by M. Daguerre, who had been occupied with this subject from 1826, if not earlier, is another remarkable instance of the decomposing effects of the solar rays. A clean and highly polished plate of silvered copper is exposed for a certain period to the vapor of iodine, and then transported to the camera obscura. In the most improved state of the process, a very short time suffices for effecting the necessary change in the film of silver iodide. The picture, however, only becomes visible by exposing it to the vapor of mercury, which attaches itself, in the form of exceed-

ingly minute globules, to those parts which have been most acted upon, that is to say, to the lights, the shadows being formed by the dark polish of the metallic plate. Lastly, the drawing is washed with sodium hyposulphite, to remove the undecomposed silver iodide and render it permanent.

The images of objects thus produced bear the most minute examination with a magnifying glass, the smallest details being depicted with perfect fidelity.

Great improvements have been necessarily made in the application of this beautiful art to taking portraits. By the joint use of bromine and iodine the plates are rendered far more sensitive, and the time of sitting is shortened to a very few seconds. In fact, the sensitiveness of the photographic plate has been so increased, that excellently defined pictures of objects in rapid motion, horses jumping, ships sailing, &c., have been obtained. When the operation is completed, the color of the plate is much improved by the deposition of an exceedingly thin film of gold, which communicates a warm purplish tint, and removes the previous dull leaden-gray hue, to most persons very offensive.

The difficulty of obtaining good paper for the talbotype has led to the invention of various substitutes: albumen on glass and *collodion* are used with success; a soluble iodide, or some analogous salt, is mixed with either liquid, and the mixture applied to a glass or porcelain plate, dried, and immersed in a solution of silver nitrate; thus a sensitive coating is formed, upon which the images of the camera or microscope are thrown, and developed by subsequent treatment with deoxidizing agents, — either pyrogallic acid, gallic acid, or a ferrous salt may be used. The fixing is accomplished by sodium hyposulphite. The result is either negative or positive at the will of the operator. The proofs on porcelain or glass may be burned in, and perhaps thus rendered indestructible by time.

Etching and lithographic processes, by combined chemical and photographic agency, promise to be of considerable utility. The earliest is that of Niepce: he applied a bituminous coating to a metal plate, upon which an engraving was superimposed. The light being thus partially interrupted, acted unequally upon the varnish; a liquid hydro-carbon, *petroleum*, used as a solvent, removed the bitumen wherever the light had not acted; an engraving acid could now bite the unprotected metal, which could eventually be printed from in the usual way. Dr. Donné and Dr. Berres, by submitting the daguerreotype to the action of nitric acid and its vapor, obtained etchings from which proofs could be taken. Mr. Grove, by using chlorine evolved by voltaic agency, succeeded in obtaining a more manageable process Very successful results have also been obtained by M. Fizeau, who submits the daguerreotype to the action of a mixture of dilute nitric acid, common salt, and potassium nitrate, when the silver only is attacked, the mercurialized portion of the image resisting the acid; an etching is thus obtained following minutely the lights and shadows of the picture. To deepen this etching, the silver chloride formed is removed by ammonia, the plate is boiled in caustic potassa and again treated with acid, and so on till the etching is of sufficient depth. In extreme cases electro-gilding is resorted to, and an engraving acid used to get still more powerful impressions.

Among the latest results are those obtained by Mr. Talbot on steel plates: he uses a mixture of potassium bichromate and gelatin, which hardens by exposure to the light; the parts not affected are removed by washing. Platinum tetrachloride is used as an etching liquid; it has the advantage of biting with greater regularity than nitric acid.

The bitumen process of M. Niepce has been applied to lithographic stone; and positives obtained from negative talbotypes have been printed off by a modification of the ordinary lithographic process. M. Niepce finds that ether dissolves the altered bitumen, while naphtha, or benzol, attacks by preference the bitumen in its normal condition.

RADIATION, REFLECTION, ABSORPTION, AND TRANSMISSION OF HEAT.

RADIATION OF HEAT.

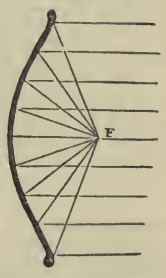
IF a red-hot ball be placed upon a metallic support, and left to itself, cooling immediately commences, and only stops when the temperature of the ball is reduced to that of the surrounding air. This effect takes place in three ways: heat is conducted away from the ball through the substance or the support; another portion is removed by the convective power of the air; and the residue is thrown off from the heated body in straight lines or rays which pass through air without interruption, and become absorbed by neighboring objects which happen to be presented to their impact.

This radiant or radiated heat resembles, in very many respects, ordinary light; it moves with great velocity; it suffers reflection from surfaces; it enters and traverses media, undergoing at the same time refraction, absorption, and polarization; in fact, it is in all these cases obedient to the same laws which regulate the corresponding phenomena in optics.

The fact of the *reflection* of heat may be very easily proved. If a person stand before a fire in such a position that his face may be screened by the mantelshelf, and if he then take a bright piece of metal, as a sheet of tinned plate, and hold it in such a manner that the fire may be seen by reflection, a distinct sensation of heat will at the same moment be felt.

The apparatus best fitted for studying these facts consists of a pair of concave metallic mirrors of the form called parabolic. The parabola is a curve possessing very peculiar properties, one of the most prominent being the following: — A tangent drawn to any part of the curve makes equal angles with two lines, one of which proceeds from the point where the tangent touches the curve in a direction parallel to what is called the axis of the parabola, and the other from the same spot through a point in front of the curve called the focus. It results from this that parallel rays, either of light or heat, falling upon a mirror of this particular curvature in a direction parallel with the axis of the parabola, will be all reflected to a single point at the focus; and rays diverging from this focus, and impinging upon the mirror, will, after reflection, become parallel (fig. 66).

Fig. 66.

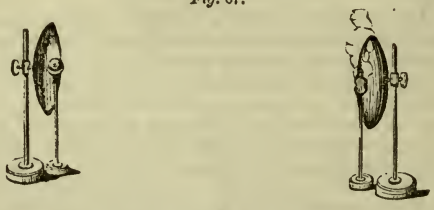


For practical purposes the parabolic reflector is generally replaced by a spherical mirror of but little extent as compared with its radius of curvature. The line drawn from the centre of the curvature to the middle of the reflector, *i. e.*, the radius of the sphere, is the *principal axis*, and the middle of this radius is the focus of the spherical reflector. This focus exhibits nearly all the characters of the focus of the parabolic reflector. The spherical reflector is much more easily constructed than the parabolic; it has, moreover, the advantage that every line drawn from the centre of the curvature towards the surface of the mirror may be

looked upon as an axis (collateral axis), and the middle of such line as a focus (collateral focus), and used as such.

If two such mirrors be placed opposite to each other at a considerable distance, and so adjusted that their axes shall be coincident, and a hot body placed in the focus of the one, while a thermometer occupies that of the other, the reflection of the rays of heat will become manifest by their effect upon the instrument. In this manner, with a pair of by no means very perfect mirrors, 18 inches in diameter, separated by an interval of 20 feet or more, amadou or gunpowder may be readily fired by a red-hot ball in the focus of the opposite mirror (fig. 67).

Fig. 67.



The power of radiation varies exceedingly with different bodies, as may be easily proved. If two similar vessels of equal capacity, and constructed of thin metal, one having its surface highly polished, while that of the other is covered with lampblack, be filled with hot water of the same temperature, and their rate of cooling observed from time to time with a thermometer, it will be constantly found that the blackened vessel loses heat much faster than the one with bright surfaces; and since both are put on a footing of equality in other respects, this difference, which will often amount to many degrees, must be ascribed to the superior emissive power of the film of soot.

By another arrangement, a numerical comparison can be made of these differences. A cubical metallic vessel is prepared, each of whose sides is in a different condition, one being polished, another rough, a third covered with lampblack, &c. The vessel is filled with water, kept constantly at 100° by a small steam-pipe. Each of its sides is then presented in succession to a good concave mirror, having in its focus one of the bulbs of the differential thermometer before described (fig. 26), the bulb itself being blackened. The effect produced on this instrument is taken as a measure of the comparative radiating powers of the different surfaces. Sir John Leslie obtained by this method of experimenting the following results:

	Emissive power.		Emissive power.
Lampblack	100	Tarnished lead	45
Writing-paper	98	Clean lead	19*
Glass	90	Polished iron	15
Graphite	75	Polished silver	12

* The supposed influence of mere difference of surface has been called in question by Melloni, who attributes to other causes the effects observed by Leslie and others, among which superficial oxidation and differences of physical condition with respect to hardness and density are among the most important. With metals not subject to tarnish, scratching the surface *increases* the emissive power when the plates have been rolled or hammered, *i. e.*, are in a compressed state, and diminishes it, on the contrary, when the metal has been cast and carefully polished without burnishing. In the case of ivory, marble, and jet, where compression cannot take place, no difference is perceptible in the radiating power of polished and rough surfaces. (Ann. Ch. Phys., lxx. 435.)

The best reflecting surfaces are always the worst radiators; polished metal reflects nearly all the heat that falls upon it, while its radiating power is the feeblest of any substance tried, and lampblack, which reflects nothing, radiates most perfectly.

The power of *absorbing* heat is in direct proportion to the power of emission. The polished metal mirror, in the experiment with the red-hot ball, remains quite cold, although only a few inches from the latter; or, again, if a piece of gold leaf be laid upon paper, and a heated iron held over it until the paper is completely scorched, it will be found that the film of metal has perfectly defended that portion beneath it.

The faculty of absorption seems to be a good deal influenced by color. Dr. Franklin found that when pieces of cloth of various colors were placed on snow exposed to the feeble sunshine of winter, the snow beneath became unequally melted, the effect being always in proportion to the depth of the color; and Dr. Stark has since obtained a similar result by a different method of experimenting. According to the late researches of Melloni, this effect depends less on the color than on the nature of the coloring matter which covers the surface of the cloth. According to Melloni, color does not influence absorption when the heat rays are emitted from a non-luminous source, such as a cube filled with hot water; it has, however, great effect on the absorption of heat rays given off from a luminous body, as the sun, &c.

These facts afford an explanation of two very interesting and important natural phenomena, namely, the origin of dew, and the cause of the land- and sea-breezes of tropical countries. While the sun remains above the horizon, the heat radiated by the surface of the earth into space is compensated by the absorption of the solar beams; but when the sun sets, and the supply ceases, while the emission of heat goes on as actively as before, the surface becomes cooled until its temperature sinks below that of the air. The air in contact with the earth of course participates in this reduction of temperature; the aqueous vapor present speedily reaches its point of maximum density, and then begins to deposit moisture, whose quantity will depend upon the proportion of vapor in the atmosphere, and on the extent to which the cooling process has been carried.

It is observed that dew is most abundant in a clear calm night, succeeding a hot day: under these circumstances the quantity of vapor in the air is usually very great, and at the same time radiation proceeds with most facility. At such times a thermometer laid on the ground will, after some time, indicate a temperature of 5°, 8°, or even 10° below that of the air a few feet higher. Clouds hinder the formation of dew by reflecting back to the earth the heat radiated from its surface, and thus preventing the necessary reduction of temperature; and the same effect is produced by a screen of the thinnest material stretched at a little height above the ground. In this manner gardeners often preserve delicate plants from destruction by the frosts of spring and autumn. The piercing cold felt just before and at sunrise, even in the height of summer, is the consequence of this refrigeration having reached its maximum.

Wind also effectually prevents the deposition of dew, by constantly renewing the air lying upon the earth before it has had its temperature sufficiently reduced to cause condensation of moisture.

Many curious experiments may be made by exposing on the ground at night bodies which differ in their powers of radiation. If a piece of black cloth and a plate of bright metal be thus treated, the former will be often found in the morning covered with dew, while the latter remains dry.

Land and sea breezes are certain periodical winds common to most sea-coasts within the tropics, but by no means confined to those regions. It is observed that a few hours after sunrise a breeze springs up at sea, and

blows directly on shore, and that its intensity increases as the day advances, and declines and gradually expires near sunset. Shortly afterwards a wind arises in exactly the opposite direction, namely, from the land towards the sea, lasts the whole of the night, and only ceases with the reappearance of the sun.

It is easy to give an explanation of these effects. When the sun shines at once upon the surface of the earth and that of the sea, the two become unequally heated, because the water, although it possesses greater power of absorbing heat, is yet more slowly warmed, in consequence of its greater capacity for heat, and the greater depth to which the rays of the sun can penetrate. The air over the heated surface of the ground, being expanded by heat, rises, and has its place supplied by colder air flowing from the sea, producing the sea-breeze. When the sun sets, both sea and land begin to cool by radiation: the rate of cooling of the latter will, however, far exceed that of the former, and its temperature will rapidly fall. The air above becoming cooled and condensed, flows outwards in obedience to the laws of fluid pressure, and displaces the warmer air of the ocean. In this manner, by an interchange of air between sea and land, the otherwise oppressive heat is moderated, to the great advantage of those who inhabit such localities. The land and sea breezes extend to a small distance only from shore, but afford, notwithstanding, essential aid to coasting navigation, since vessels on either tack enjoy a fair wind during the greater part of both day and night.

TRANSMISSION OF HEAT; DIATHERMANCY.

Rays of heat, in passing through air, receive scarcely more obstruction than those of light under similar circumstances; but with other transparent media the case is different. If a parabolic mirror be taken, and its axis directed towards the sun, the rays both of heat and light will be reflected to the focus, which will exhibit a temperature sufficiently high to fuse a piece of metal, or fire a combustible body. If a plate of glass be now placed between the mirror and the sun, the effect will be perceptibly diminished.

Now, let the same experiment be made with the heat of a kettle filled with boiling water; the heat will be concentrated by reflection as before, but, on interposing the glass, the heating effect at the focus will be reduced to nothing. Thus, the rays of heat coming from the sun traverse even glass in considerable quantity, but not so easily as air, whilst rays from hot water are entirely stopped by glass.

In the year 1833, M. Melloni published the first of a series of exceedingly valuable researches on this subject, which are to be found in detail in various volumes of the Annales de Chimie et de Physique.* It will be necessary, in the first instance, to describe the method of operation followed by this philosopher.

Not long before, two very remarkable facts had been discovered: Orsted, in Copenhagen, showed that a current of electricity, however produced, exercises a singular and perfectly definite action on a magnetic needle; and Seebeck, in Berlin, found that an electric current may be generated by the unequal effects of heat on different metals in contact. If a wire conveying an electrical current be brought near a magnetic needle, the latter will immediately alter its position and assume a new one as nearly perpendicular to the wire as the mode of suspension and the magnetism of the earth will permit. When the wire, for example, is placed directly over the needle

Fig. 68.

* Translated also in Taylor's "Scientific Memoirs."

and parallel to its length, while the current it carries travels from north to south, the needle is deflected from its ordinary direction, and the north pole driven to the eastward. When the current is reversed, the same pole deviates to an equal amount towards the west. Placing the wire below the needle instead of above, produces the same effect as reversing the current.

When the needle is subjected to the action of two currents in opposite directions, the one above and the other below, they will obviously concur in their effects. The same thing happens when the wire carrying the current is bent upon itself, and the needle placed between the two portions; and since every time the bending is repeated, a fresh portion of the current is made to act in the same manner upon the needle, it is easy to see how a current, too feeble to produce any effect when a simple straight wire is employed, may be made by this contrivance to exhibit a powerful action on the magnet. It is on this principle that instruments called *galvanometers*, *galvanoscopes*, or *multipliers*, are constructed; they serve not only to indicate the existence of electrical currents, but to show, by the effects upon the needle, the direction in which they are moving. The delicacy of the instrument can be extraordinarily increased by the use of a very long coil of wire and two needles of equal strength, and with opposite poles conjoined (fig. 82). These needles are hung by untwisted silk, one between the coils and the other above them, so that the current acts in the same direction on both. The thickness of the wire has some influence on the delicacy of the instrument. For the following experiments it should not be less than $\frac{1}{24}$ of an inch thick.

Fig. 69.

Where two pieces of different metals, connected together at each end, have one of their joints more heated than the other, an electric current is immediately set up. Of all the metals tried, bismuth and antimony form the most powerful combination. A single pair of bars having one of their junctions heated in the manner shown (fig. 70), can develop a current strong enough to deflect a compass-needle placed within; and, by arranging a number in a series and heating their alternate ends, the intensity of the current may be very much increased. Such an arrangement is called a thermo-electric pile. Melloni constructed a very small thermo-electric pile of this kind, containing fifty-five slender bars of bismuth and antimony, laid side by side and soldered together at their alternate ends, as shown in natural size in fig. 71. He connected this pile with an exceedingly delicate multiplier, and found himself in the possession of an instrument for measuring small variations of temperature, far surpassing in delicacy the air-thermometer in its most sensitive form, and having great advantages in other respects over that instrument when employed for the purposes to which he devoted it.

Fig. 70.

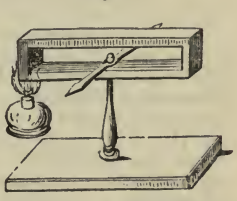
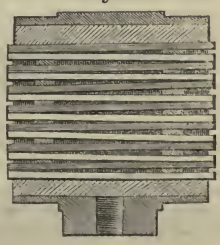


Fig. 71.

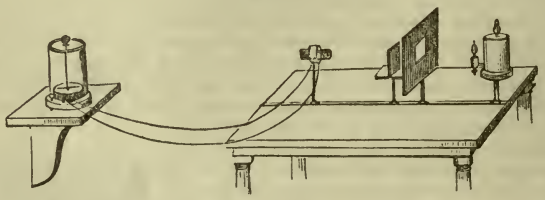


The substances whose powers of transmission were to be examined were cut into plates of a determinate thickness, and, after being well polished, arranged in succession in front of the little pile, the extremity of which was blackened

to promote the absorption of the rays. A perforated screen, the area of whose aperture equalled that of the face of the pile, was placed between the source of heat and the body under trial, while a second screen served to intercept all radiation until the moment of the experiment.

After much preliminary labor, for the purpose of testing the capabilities of the apparatus and the value of its indications, an extended series of

Fig. 72.



researches was undertaken and carried on during a long period with great success; some of the most curious results are given in the annexed table.

Four different sources of heat were employed in these experiments, differing in their nature and in their degrees of intensity: the naked flame of an oil-lamp; a coil of platinum wire heated to redness; blackened copper at 390°; and the same heated to 100°.

Substances. (Thickness of plate 0·1 inch, nearly.)	Transmission of 100 rays of heat from			
	Oil-lamp.	Red-hot Platinum.	Copper at 734° (390° C.)	Copper at 212° (100° C.)
Rock-salt, transparent and colorless	92	92	92	92
Fluor-spar, colorless	78	69	42	33
Rock-salt, muddy	65	65	65	65
Beryl	54	23	13	0
Fluor-spar, greenish	46	38	24	20
Iceland spar	39	28	6	0
Plate-glass	39	24	6	0
Rock-crystal	38	28	6	0
Rock-crystal, brown	37	28	6	0
Tourmaline, dark-green	18	16	3	0
Citric acid, transparent	11	2	0	0
Alum, transparent	9	2	0	0
Sugar-candy	8	0	0	0
Fluor-spar, green, translucent	8	6	4	3
Ice, pure and transparent	6	0	0	0

On examining this remarkable table, which is an abstract of one much more extensive, the first thing that strikes the eye is the want of connection between the power of transmitting heat and that of transmitting light. Taking, for instance, the oil-lamp as the source of heat: out of the quantity of heat represented by 100 rays falling upon the pile, the proportion

transmitted by similar plates of rock-salt, glass, and alum, may be expressed by the numbers, 92, 39, and 9; and yet these bodies are equally transparent with respect to light. Generally speaking, color was found to interfere with the transmissive power, but to a very unequal extent: thus, in fluor-spar, colorless, greenish, and deep green, the quantities transmitted were 78, 46, and 8, while the difference between colorless and brown rock-crystal was only 1. Bodies absolutely opaque, as wood, metals, and black marble, stopped the rays completely, although it was found that the faculty of transmission was possessed, to a certain extent, by some which were nearly in that condition, as thick plates of brown quartz, black mica, and black glass.

A great difference is noticed in heat-rays derived from different sources. Out of 100 rays from each source which fell on rock-salt, the same proportion was always transmitted whether the rays proceeded from the intensely heated flame, the red-hot platinum wire, or the copper at 390° or 100°; but this is true of no other substance in the list. In the case of plate-glass, we have the numbers 39, 24, 6, and 0 as representatives of the comparative quantities of heat transmitted through the plate from each source; or in three varieties of fluor-spar, as in the following statement:

	Flame.	Red heat.	390°.	100°.
Colorless . .	78	69	42	33
Greenish . .	46	38	24	20
Dark green . .	8	6	4	3

One substance, beryl, out of 100 rays from the intensely heated source, suffers 54 to pass; and out of the same number (that is, an equal quantity of heat) from metal at 100° none at all; whilst another substance, fluor-spar, transmits rays from the two sources mentioned in the proportion of 8 to 3.

These, and many other curious phenomena, are fully and completely explained on the supposition, that among the invisible rays of heat differences are to be found exactly analogous to those differences between rays of light which we are accustomed to call colors. Rock-salt and air are the only substances yet known which are truly *diathermanous*, or equally transparent to all kinds of heat-rays: they are to the latter what white glass or water is to light; they suffer rays of every description to pass with equal facility. All other bodies act like colored glasses, absorbing certain rays more abundantly than the rest, and *coloring*, as it were, the heat which passes through them.

These heat-tints have no direct relation to ordinary colors; their existence is, nevertheless, almost as clearly made out as that of the colored rays of the spectrum. Bodies at a comparatively low temperature emit rays of such a tint only as to be transmissible by a few substances: as the temperature rises, rays of other heat-colors begin to make their appearance, and transmission of some portion of these rays takes place through a great number of bodies; while at the temperature of intense ignition we find rays of all colors thrown out, some of which will certainly find their way through a great variety of substances. The kind of rays emitted by different bodies of the same temperature is by no means the same, but seems materially to depend on the nature of the radiating body. When a bundle of heterogeneous rays passes through a medium, those of one kind are powerfully absorbed, while those of another are not affected. By their transmission through the body the rays have undergone a sifting; if now these sifted rays be passed through a second plate of the same medium, a much smaller proportional loss will occur than in the case of the first plate, because the rays which the medium readily takes up are mostly wanting,

while those which easily pass through the body in question are present in more notable quantity. The same thing happens when a number of plates are interposed; the rays after traversing one plate are but little interrupted by others of a similar nature.

By cutting rock-salt into prisms and lenses, it is easy to show that radiated heat may be refracted like ordinary light, and its beams made to converge or diverge at pleasure; and, lastly, to complete the analogy, it has been shown to manifest the phenomena of interference, and to be susceptible of polarization by transmission through plates of double-refracting minerals, in the manner as light itself.

The absorptive power of gases and vapors for rays of heat by which they are traversed had long been neglected; and it is only recently that we have become indebted to Professor Tyndall and Professor Magnus for some researches upon this subject. The absorptive power of perfectly dry air, of oxygen, nitrogen, and hydrogen in the state of purity is very small; the absorptive power of compound gases and vapors, *e. g.* of water-vapor, carbonic oxide, carbonic acid, and more especially of olefiant gas, ammonia, and the vapors of volatile oils, is much greater. The following table gives, according to Tyndall, the relative absorptive powers of different gases for dark rays of heat emanating from copper at 270°, when the gases are examined under a pressure of one atmosphere:—

Atmospheric air	1	Carbon dioxide	90
Oxygen	1	Nitrogen monoxide	355
Nitrogen	1	Hydrogen sulphite	390
Hydrogen	1	Marsh gas	403
Chlorine	39	Sulphurous oxide	710
Hydrochloric acid	62	Olefiant gas	970
Carbon monoxide	90	Ammonia	1195

The absorptive power of a gas increases with an increases of the density, but is, in the case of gases endowed with a high absorptive power, by no means proportionate to the density.

Rays of heat of the above description are not capable of passing through a tube 3 feet long filled with ammonia of the ordinary pressure of the atmosphere; such a layer of ammonia, though quite colorless and transparent to light, is perfectly impermeable (it might be said black) to heat. The clement chlorine, though colored and less transparent to light, allows the rays of heat to pass more freely than the compound hydrochloric acid, which is colorless and more transparent to light. These examples show that the absorptive power of gases for rays of heat is perfectly independent of that for rays of light.

From Tyndall's experiments it appears also that vapor of water, weight for weight, transcends all other gases in heat-absorbing power; so much, indeed, that the aqueous vapor in the air, though not amounting on the average to more than 0·45 per cent. of the whole, exerts an absorptive action on heat-rays many times greater than the air through which it is diffused. This great absorbing power of water-vapor has a powerful effect in checking the cooling down of the earth's surface by radiation; and it is in great part from this cause that in moist climates, like that of England, the range of temperature between night and day, and between summer and winter, is so much less than in drier climates under the same latitude.

It has been established by experiment, and likewise theoretically demonstrated by Kirchhoff, that of two bodies, the one which has the greater power of absorbing rays of heat, possesses also the greater power of radiating them, and that the law mentioned on page 92, according to which the power of absorbing heat is in direct proportion to the power of emission, holds good also for gases.

MAGNETISM.

A PARTICULAR species of iron ore has long been remarkable for its property of attracting small pieces of iron, and causing them to adhere to its surface; it is called loadstone, or magnetic iron ore.

If a piece of this loadstone be carefully examined, it will be found that the attractive force for particles of iron is greatest at certain particular points of its surface, while elsewhere it is much diminished or even altogether absent. These attractive points are denominated poles, and the loadstone itself is said to be endowed with magnetic polarity.

If one of the pole-surfaces of a natural loadstone be rubbed in a particular manner over a bar of steel, its characteristic properties will be communicated to the bar, which will then be found to attract iron-filings like the loadstone itself. Further, the attractice force will appear to be greatest at two points situated very near the extremities of the bar, and least of all towards the middle. The bar of steel so treated is said to be magnetized, or to constitute an artificial magnet.

When a magnetized bar or natural magnet is suspended at its centre in any convenient manner, so as to be free to move in a horizontal plane, it is always found to assume a particular direction with regard to the earth, one end pointing nearly north and the other nearly south. If the bar be moved from this position, it will tend to reassume it, and, after a few oscillations, settle at rest as before. The pole which points towards the astronomical north is usually distinguished as the north pole of the bar, and that which points southward, as the south pole. A suspended magnet, either natural or artificial, of symmetrical form, serves to exhibit certain phenomena of attraction and repulsion in the presence of a second magnet, which deserve particular attention. When a north pole is presented to a south pole, or a south pole to a north, attraction ensues between them; the ends of the bars approach each other, and, if permitted, adhere with considerable force; when, on the other hand, a north pole is brought near a second north pole, or a south pole near another south pole, mutual repulsion is observed, and the ends of the bars recede from each other as far as possible. *Poles of an opposite name attract, and of a similar name repel each other.* Thus, a small bar or needle of steel, properly magnetized and suspended, and having its poles marked, becomes an instrument fitted not only to discover the existence of magnetic power in other bodies, but to estimate the kind of polarity affected by their different parts.

A piece of soft iron brought into the neighborhood of a magnet acquires itself magnetic properties: the intensity of the power thus conferred depends upon that of the magnet and upon the interval which divides the two, becoming greater as that interval decreases, and greatest of all when in actual contact. The iron, under these circumstances, is said to be magnetized by induction or influence, and the effect, which in an instant reaches its maximum, is at once destroyed by removing the magnet.

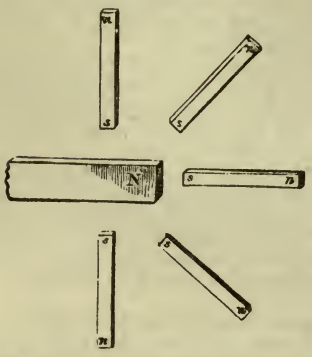
When steel is substituted for iron in this experiment, the inductive action is hardly perceptible at first, and only becomes manifest after the lapse of a certain time: in this condition, when the steel bar is removed from the magnet, it retains a portion of the induced polarity. It becomes, indeed,

a permanent magnet, similar to the first, and retains its peculiar properties for an indefinite period.

A particular name is given to this resistance which steel always offers in a greater or less degree both to the development of magnetism and its subsequent destruction; it is called *specific coercive power.*

The rule which regulates the induction of magnetic polarity in all cases is exceedingly simple, and most important to be remembered. The pole produced is always of the opposite name to that which produced it, a north pole developing south polarity, and a south pole north polarity. The north pole of the magnet figured in the sketch induces south polarity in all the nearer extremities of the pieces of iron or steel which surround it, and a state similar to its own in all the more remote extremities. The iron thus magnetized is capable of exerting a similar inductive action on a second piece, and that upon a third, and so to a great number, the intensity of the force diminishing as the distance from the permanent magnet increases. It is in this way that a magnet is enabled to hold up a number of small pieces of iron, or a bunch of filings, each separate piece becoming a magnet for the time by induction.

Fig. 73.



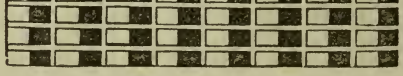
Magnetic polarity, similar in degree to that which iron presents, has been found only in some of the compounds of iron, in nickel and in cobalt.

Magnetic attractions and repulsions are not in the slightest degree interfered with by the interposition of substances destitute of magnetic properties. Thick plates of glass, shellac, metals, wood, or of any substances except those above mentioned, may be placed between a magnet and a suspended needle, or a piece of iron under its influence, the distance being preserved, without the least perceptible alteration in its attractive power, or force of induction.

One kind of polarity cannot be exhibited without the other. In other words, a magnetic pole cannot be insulated. If a magnetized bar of steel be broken at its neutral point, or in the middle, each of the broken ends acquires an opposite pole, so that both portions of the bar become perfect magnets; and, if the division be carried still further, if the bar be broken into a hundred pieces, each fragment will be a complete magnet, having its own north and south poles.

This experiment serves to show very clearly that the apparent polarity of the bar is the consequence of the polarity of each individual particle,

Fig. 74.



the poles of the bar being merely points through which the resultants of all these forces pass; the largest magnet is made up of an immense number

of little magnets regularly arranged side by side, all having their north poles looking one way, and their south poles the other. The middle portion of such a system cannot possibly exhibit attractive or repulsive effects on an external body, because each pole is in close juxtaposition with one of an opposite name and of equal power; hence their forces will be exerted in opposite directions and neutralize each other's influence. Such will not be the case at the extremities of the bar; there uncompensated polarity will be found capable of exerting its specific power.

This idea of regular polarization of particles of matter in virtue of a pair of opposite and equal forces, is not confined to magnetic phenomena; it is the leading principle in electrical science, and is constantly reproduced in some form or other in every discussion involving the consideration of molecular forces.

Artificial steel magnets are made in a great variety of forms; such as small light needles, mounted with an agate cap for suspension upon a fine point; straight bars of various kinds; bars curved into the shape of a horse-shoe, &c. All these have regular polarity communicated to them by certain processes of rubbing or touching with another magnet, which require care, but are not otherwise difficult of execution. When great power is wished for, a number of bars may be screwed together, with their similar ends in contact, and in this way it is easy to construct permanent steel magnets capable of sustaining great weights. To prevent the gradual destruction of magnetic force, which would otherwise occur, it is usual to arm each pole with a piece of soft iron or keeper, which, becoming magnetized by induction, serves to sustain the polarity of the bar, and in some cases even increases its energy.

The direction spontaneously assumed by a suspended needle indicates that the earth itself has the properties of an enormous magnet, whose south magnetic force is concentrated in the northern hemisphere. A line joining the two poles of such a needle or bar indicates the direction of the so-called *magnetic meridian* of the place, which is a vertical plane coincident with the direction of the needle.

The magnetic meridian of a place is not usually coincident with its geographical meridian, but makes with the latter a certain single called the *declination* of the needle.

The amount of the declination of the needle from the true north and south not only varies at different places, but in the same place is subject to daily, yearly, and secular fluctuations, which are called the variations of declination. Thus, at the commencement of the 17th century, the declination, in London, was eastward; in 1660 it was 0; that is, the needle pointed due north and south. Afterwards it became westerly, slowly increasing until the year 1818, when it reached 24° 30′, since which time it has been slowly diminishing, and, in the present year (1868) it is 20° 10′.

Of late the march of the daily variations of declination has been carefully compared with the positions of the sun as well as the moon at the corresponding period. This inquiry, suggested by General Sabine, and carried on for a number of years in several localities, has led to the remarkable result that these celestial bodies exert a definite influence upon the magnetic needle, and must therefore be considered as magnets, like the earth itself.

If a steel bar be supported on a horizontal axis passing exactly through its centre of gravity, it will of course remain equally balanced in any position in which it may happen to be placed; if the bar so adjusted be then magnetized, it will be found to take a permanent direction, the north pole being downwards, and the bar making, in London, an angle of about 68°, with a horizontal plane passing through the axis. This is called the *dip* or *inclination* of the needle, and shows the direction in which the force

of terrestrial magnetism is most energetically exerted. The amount of this dip is different in different latitudes. Near the equator it is very small, the needle remaining nearly or quite horizontal; as the latitude increases, the dip becomes more decided; and over the magnetic pole the bar becomes completely vertical. Such a situation is, in fact, to be found in the northern hemisphere, considerably south of the geographical pole, on the west coast of Boothia Felix, lat. 70° 5′ N. and long. 96° 46′ W.; the dipping-needle has here been seen to point directly downwards, while the horizontal or compass-needle ceased to traverse. In the southern hemisphere it is the south pole which dips. The position of the south magnetic pole has been determined by the observations of Captain James Ross to be about lat. 73° S. and long. 130° E.

By observing a great number of points near the equator in which the dip becomes reduced to nothing, a line, cutting the equator in two points, may be traced around the earth, called the magnetic equator, and on both sides, a number of smaller closed curves called lines of equal dip. These lines present great irregularities when compared with the equator itself and the parallels of latitude, the magnetic equator deviating from the terrestrial one as much as 12° at its point of greatest divergence. Like the horizontal declination, the dip is also subject to change at the same place. Observations have not yet been made during sufficient time to determine accurately the law and rate of alteration, and great practical difficulties exist also in the construction of the instruments. In the year 1773, it was about 72°: in London at the present time it is 67° 57′.

The inductive power of the magnetism of the earth may be shown by holding in a vertical position a bar of very soft iron; the lower end will be found to possess north polarity, and the upper, the contrary state. On reversing the bar, the poles are also reversed. All masses of iron whatever, when examined by a suspended needle, will be found in a state of magnetic polarity by the influence of the earth; iron columns, tools in a smith's shop, fire-irons, and other like objects, are all usually magnetic, and those made of steel permanently so. On board ship, the presence of so many large masses of iron — guns, anchors, water-tanks, &c., — thus polarized by the earth, causes a derangement of the compass-needles to a very dangerous extent: happily a plan has been devised for determining the amount of this local attraction in different positions of the ship, and making suitable corrections.

The mariner's compass, which is nothing more than a suspended needle attached to a circular card marked with the points, was not in general use in Europe before the year 1300, although the Chinese have had it from very early antiquity. Its value to the navigator is now very much increased by correct observations of the exact amount of the declination in various parts of the world.

Probably every substance in the world contributes something to the magnetic action of the earth; for according to the latest discoveries of Faraday, magnetism is not peculiar to those substances which have more especially been called magnetic, such as iron, nickel, cobalt; but it is the property of all metals, though to a much smaller degree. Very powerful magnets are required to show this remarkable fact. Large horse-shoe magnets, made by the action of the electric current, are most proper. The magnetic action on different substances which are capable of being easily moved, differs not only according to the size, but also according to the nature of the substance. In consequence of this, Faraday divides all bodies into two classes. He calls the one magnetic, or, better, *paramagnetic*, and the other *diamagnetic*.

The matter of which a paramagnetic (magnetic) body consists is attracted by both poles of the horse-shoe magnet; on the contrary, the matter of a

diamagnetic body is repelled. When a small iron bar is hung by untwisted silk between the poles of the magnet, so that its long diameter can easily move in a horizontal plane, it arranges itself axially, that is, parallel to the straight line which joins the poles, or to the magnetic axis of the poles; assuming at the end which is nearest the north pole, a south pole, and at the end nearest the south pole, a north pole. Whenever the little bar is removed from this position, after a few oscillations, it returns again to its previous position. The whole class of paramagnetic bodies behave in a precisely similar way under similar circumstances; but in the intensity of the effects great differences occur.

Diamagnetic bodies, on the contrary, have their long diameters placed equatorially, that is, at right angles to the magnetic axis. They behave, as if at the end opposite to each pole of the magnet the same kind of polarity existed.

In the first class of substances, besides iron, which is the best representative of the class, we have nickel, cobalt, manganese, chromium, cerium, titanium, palladium, platinum, osmium, aluminium, oxygen, and also most of the compounds of these bodies; most of them, even when in solution. According to Faraday, the following substances are also feebly paramagnetic (magnetic): paper, sealing-wax, Indian-ink, porcelain, asbestos, fluor-spar, minium, cinnabar, binoxide of lead, sulphate of zinc, tourmaline, graphite, and charcoal.

In the second class are placed bismuth, antimony, zinc, tin, cadmium, sodium, mercury, lead, silver, copper, gold, arsenic, uranium, rhodium, iridium, tungsten, phosphorus, iodine, sulphur, chlorine, hydrogen, and many of their compounds. Also, glass free from iron, water, alcohol, ether, nitric acid, hydrochloric acid, resin, wax, olive oil, oil of turpentine, caoutchouc, sugar, starch, gum, and wood. These are diamagnetic.

If diamagnetic and paramagnetic bodies are combined, their peculiar properties are destroyed. In most of these compounds, occasionally, in consequence of the presence of the smallest quantity of iron, the peculiar magnetic power remains more or less in excess. Thus green bottle-glass and many varieties of crown glass are magnetic in consequence of the iron they contain.

In order to examine the magnetic properties of fluids, they are placed in very thin glass tubes, the ends of which are then closed by melting; they are then hung horizontally between the poles of the magnet. Under the influence of poles sufficiently powerful, they begin to swing, and according as the fluid contents are paramagnetic (magnetic) or diamagnetic, they assume an axial or equatorial position.

Faraday has tried the magnetic condition of gases in different ways. One method consisted in making soap-bubbles with the gas which he wished to investigate, and bringing these near the poles. Soap and water alone is feebly diamagnetic. A bubble filled with oxygen was strongly attracted by the magnet. All other gases in the air are diamagnetic, that is, they are repelled. But, as Faraday has shown, in a different way, this partly arises from the paramagnetic (magnetic) property of the air. Thus he found that nitrogen, when this differential action was eliminated, was perfectly indifferent, whether it was condensed or rarefied, whether cooled or heated. When the temperature is raised, the diamagnetic property of gases in the air is increased. Hence the flame of a candle or of hydrogen is strongly repelled by the magnet. Even warm air is diamagnetic in cold air.

For some time it had been believed that bodies in a crystalline form had a special and peculiar behavior when placed between the poles of a magnet. It appeared as though the magnetic directing power of the crystal had some peculiar relation to the position of its optic axis; so that, inde-

pendently of the magnetic property of the substance of the crystal, if the crystal was positively optical, it possessed the power of placing its optic axis parallel with the line which joined the poles of the magnet, while optically negative crystals tried to arrange their axis at right angles to this line. This supposition is disproved by the excellent investigation of Tyndall and Knoblauch, who showed that exceptions to the above law are furnished by all classes of crystals, and proved that the action, instead of being independent of the magnetic nature of the mass, was completely reversed where, in isomorphous crystals, a magnetic constituent was substituted for a diamagnetic one. Rejecting the various new forces assumed, Tyndall and Knoblauch referred the observed phenomena to the modification of the magnetic force by structure, and they imitated the effects exactly, by means of substances whose structure had been modified by compression. In a later investigation, Tyndall demonstrated the fundamental principle on which these phenomena depend, showing that the *entire mass* of a magnetic body is most strongly attracted when the attracting force acts parallel to the line of compression; and that a diamagnetic substance is most strongly repelled when the repulsion acts along the same line. Hence when such a body is freely suspended in the magnetic field, the line of compression must set axial or equatorial, according as the mass is magnetic or diamagnetic. Faraday was the first to establish a differential action of this kind in the case of bismuth; Tyndall extended it to several magnetic and diamagnetic crystals, and showed that it was not confined to them, but was a general property of matter. It was also proved that for a fixed distance the attraction of a magnetic sphere, and the repulsion of a diamagnetic sphere, followed precisely the same law, both being exactly proportioned to the square of the exciting current.

The phenomena of diamagnetism naturally suggest the inquiry, whether the repulsion exerted by a magnetic pole on diamagnetic bodies is a force distinct from that of magnetism as exerted upon iron and other bodies of the magnetic class; or whether, on the other hand, the magnetic and diamagnetic conditions of matter are merely relative, so that all bodies are magnetic in different degrees, and the apparent repulsion of a diamagnetic body, such as bismuth, is merely the result of its being attracted by the magnet less than the particles of the surrounding medium, just as a balloon recedes from the earth because its weight is less than that of an equal bulk of the surrounding air. It is easy to show that the same body may appear magnetic or diamagnetic, according to the medium in which it is placed. Ferrous sulphate is a magnetic substance, and water is diamagnetic: hence it is possible, by varying the strength of an aqueous solution of this salt, to make it either magnetic, indifferent, or diamagnetic when suspended in air. Again, a tube containing a solution of ferrous protosulphate suspended horizontally within a jar also filled with a solution of the same salt, and placed between the poles of two powerful electro-magnets, will place itself axially or equatorially, according as the solution contained in it is stronger or weaker than that in the jar. In the same manner, then, we may conceive that bismuth places itself equatorially between two magnetic poles, because it is less magnetic than the surrounding air. But the diamagnetism of bismuth and other bodies of the same class shows itself in a vacuum as well as in air: hence, if diamagnetism is not to be regarded as a distinct force, we must suppose that the *ether* is also magnetic, and occupies in the magnetic scale the place intermediate between magnetic and diamagnetic bodies.

That a body suspended in a medium of greater magnetic susceptibility than itself will recede from a magnetic pole in its neighborhood, in consequence of the greater force with which the particles of the medium are impelled towards the magnet, is so obvious a consequence of mechanical

laws that we can scarcely avoid attributing the movements of diamagnetic bodies to the cause just mentioned; at least, when the body is suspended in air or other magnetic gas. There is, however, some difficulty in reconciling the above described phenomena of compressed and crystallized bodies with this view; and, moreover, Tyndall has shown, by a method which we cannot here describe,* that diamagnetic bodies possess opposite poles, analogous to those of magnetic bodies, each of these poles being attracted by one pole of a magnet and repelled by the other. This polarity shows decidedly that the properties of diamagnetic bodies cannot be wholly due to the differential action above mentioned; for if they were, every part of a diamagnetic body would be repelled by either pole of a magnet. Diamagnetism must therefore, for the present at least, be regarded as a force distinct from *magnetism*.

* Phil. Trans., 1855 and 1856. See also Watts's Dictionary of Chemistry, vol. iii. p. 776.

ELECTRICITY.

IF glass, amber, or sealing-wax be rubbed with a dry cloth, it acquires the power of attracting light bodies, as feathers, dust, or bits of paper: this is the result of a new and peculiar condition of the body rubbed, called electrical excitation.

If a light downy feather be suspended by a thread of white silk, and a dry glass tube, excited by rubbing, be presented to it, the feather will be strongly attracted to the tube, adhere to its surface for a few seconds, and then fall off. If the tube be now excited anew, and presented to the feather, the latter will be strongly repelled.

The same experiment may be repeated with shellac or resin; the feather in its ordinary state will be drawn towards the excited body, and, after touching, again driven from it with a certain degree of force.

Now, let the feather be brought into contact with the excited glass, so as to be repelled by that substance, and let a piece of excited sealing-wax be presented to it: a degree of attraction will be observed far exceeding that exhibited when the feather is in its ordinary state. Or, again, let the feather be made repulsive for sealing-wax, and then the excited glass be presented: strong attraction will ensue.

The reader will at once see the perfect parallelism between the effects described and some of the phenomena of magnetism, the electrical excitement having a twofold nature, like the opposite polarities of the magnet. A body to which one kind of excitement has been communicated is attracted by another body in the opposite state, and repelled by one in the same state; the excited glass and resin being to each other as the north and south poles of a pair of magnetized bars.

To distinguish these two different forms of excitement, terms are employed which, although originating in some measure in theoretical views of the nature of the electrical disturbance, may be understood by the student as purely arbitrary and distinctive: it is customary to call the electricity manifested by glass rubbed with silk *positive* or *vitreous*, and that developed in the case of shellac, and bodies of the same class rubbed with flannel, *negative* or *resinous*. The kind of electricity depends in some measure upon the nature of the surface and the quality of the rubber; smooth and perfectly clean glass, rubbed with silk, becomes positive, but when ground or roughened by sand or emery, it acquires, under the same circumstances, a negative charge. Glass dried over a gas flame and rubbed with wool is generally also negative; when dried over a fire of wood-charcoal it remains positive.

The repulsion shown by bodies in the same electrical state is taken advantage of to construct instruments for indicating electrical excitement and pointing out its kind. Two balls of elder pith, hung by threads or very fine metal wires, serve this purpose in many cases: they open out when excited, in virtue of their mutual repulsion, and show by the degree of divergence the extent to which the excitement has been carried. A pair of gold leaves suspended to a metal rod having a brass plate on its upper end constitute a much more delicate arrangement, and one of great value in all electrical investigations. The rod should be covered with a thick

coating of shellac, and it must be fastened by means of a cork, air-tight, into a glass flask. The flask must have been perfectly dried previously by warming it. These instruments are called electroscopes or electrometers:

Fig. 75.

Fig. 76.

when excited by the communication of a known kind of electricity, they show by an increased or diminished divergence, the state of an electrified body brought into their neighborhood.

One kind of electricity can no more be developed without the other than one kind of magnetism: the rubber and the body rubbed always assume opposite states, and the positive condition on the surface of a mass of matter is invariably accompanied by a negative state in all surrounding bodies.

Fig. 77.

The induction of magnetism in soft iron has its exact counterpart in electricity: a body already electrified disturbs or polarizes the particles of all surrounding substances in the same manner and according to the same law, inducing a state opposite to its own in the nearer portions, and a similar state in the more remote parts. A series of globes suspended by silk threads, in the manner represented in fig. 77, will each become electric by induction when a charged body is brought near the end of the series, like so many pieces of iron in the vicinity of a magnet, the positive half of each globe looking in one and the same direction, and the negative half in the opposite one. The positive and negative signs are intended to represent the states.

The intensity of the induced electrical disturbance diminishes with the distance from the charged body; if this be removed or discharged, all the effects cease at once.

So far, the greatest resemblance may be traced between these two sets of phenomena; but here it seems in great measure to cease. The magnetic polarity of a piece of steel can awaken polarity in a second piece in contact with it by the act of induction, and in so doing loses nothing whatever of its power: this is an effect completely different from the apparent transfer or discharge of electricity constantly witnessed, which in the air and in liquids often gives rise to the appearance of a bright spark of fire. Indeed, ordinary magnetic effects comprise two groups of phenomena only,

those, namely, of attraction and repulsion, and those of induction. But in electricity, in addition to phenomena very closely resembling these, we have the effects of *discharge*, to which there is nothing analogous in magnetism, and which takes place in an instant when any electrified body is put in communication with the earth by any one of the class of substances called conductors of electricity, all signs of electrical disturbance then ceasing.

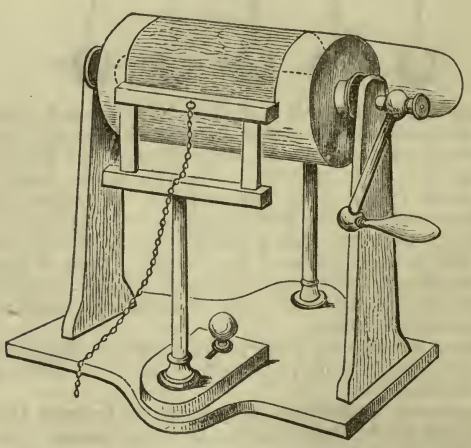
These conductors of electricity, which thus permit discharge to take place through their mass, are contrasted with another class of substances called non-conductors or insulators. The difference, however, is only one of degree, not of kind: the very best conductors offer a certain resistance to the electrical discharge, and the most perfect insulators permit it to a small extent. The metals are by far the best conductors; glass, silk, shellac, and dry gas or vapor of any sort, the very worst; and between these there are bodies of all degrees of conducting power.

Electrical discharges take place silently and without disturbance in good conductors of sufficient size. But if the charge be very intense, and the conductor very small, or imperfect from its nature, it is often destroyed with violence.

When a break is made in a conductor employed in effecting the discharge of a highly excited body, disruptive or spark-discharge, so well known, takes place across the intervening air, provided the ends of the conductor be not too distant. The electrical spark itself presents many points of interest in the modifications to which it is liable.

The time of transit of the electrical wave through a chain of good conducting bodies of great length is so minute as to be altogether inappreciable to ordinary means of observation. Professor Wheatstone's very ingenious experiments on the subject give, in the instance of motion through a copper wire, a velocity surpassing that of light.

Fig. 78.



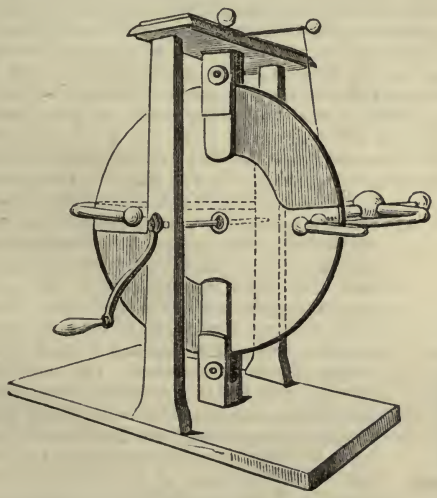
Electrical excitation is *apparent* only upon the surfaces of conductors, or those portions directed towards other objects capable of assuming the opposite state. An insulated ball charged with positive electricity, and placed in the centre of the room, is maintained in that state by the inductive action of the walls of the apartment, which immediately become nega-

tively electrified: in the interior of the ball there is absolutely no electricity to be found, although it may be constructed of open metal gauze, with meshes half an inch wide. Even on the surface the distribution of electrical force is not always the same; it depends upon the figure of the body itself, and its position with regard to surrounding objects. The polarity is always highest in the projecting extremities of the same conducting mass, and greatest of all when these are attenuated to points; in which case the inequality becomes so great that discharge takes place to the air, and the excited condition cannot be maintained.

By the aid of these principles, the construction and use of the common electrical machine, and other pieces of apparatus of great practical utility, will become intelligible.

A glass cylinder (fig. 78) is mounted with its axis in a horizontal position, and provided with a handle or winch by which it may be turned. A leather cushion is made to press by a spring against one side of the cylinder, while a large metal conducting body, armed with a number of points next the glass, occupies the other: both cushion and conductor are insulated by glass supports, and to the upper edge of the former a piece of silk is attached, long enough to reach half round the cylinder. Upon the cushion is spread a quantity of soft amalgam of tin, zinc, and mercury,* mixed up with a little grease: this substance is found by experience to excite glass most powerfully. The cylinder, as it turns, thus becomes charged by frictions against the rubber, and as quickly discharged by the row of points attached to the great conductor; and as the latter is also completely insulated, its surface speedily acquires a charge of positive electricity, which may be communicated by contact to other insulated bodies. The maximum effect is produced when the rubber is connected by a chain or wire with the

Fig. 79.



earth. If negative electricity be wanted, the rubber must be insulated and the conductor discharged.

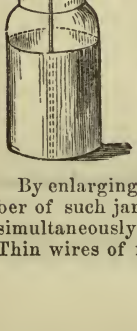
* 1 part tin, 1 zinc, and 6 mercury. An amalgam of permanent softness and great efficacy is obtained by mixing 65 parts mercury, 24 tin, and 11 zinc. It is better applied to silk than to leather.

Another form of the electrical machine consists of a circular plate of glass (fig. 79) moving upon an axis, and provided with two pairs of cushions or rubbers, attached to the upper and lower parts of the wooden frame, covered with amalgam, between which the plate moves with considerable friction. An insulated conductor, armed as before with points, discharges the plate as it turns, the rubber being at the same time connected with the ground by the wood-work of the machine, or by a strip of metal. This modification of the apparatus is preferred in all cases where considerable power is wanted.

In the practical management of electrical apparatus, great care must be taken to prevent deposition of moisture from the air upon the surface of the glass supports, which should always be varnished with fine lac dissolved in alcohol; the slightest film of water is sufficient to destroy the power of insulation. The rubbers also must be carefully dried, and, like the plate, cleansed from adhering dust before use, and the amalgam renewed if needful: in damp weather much trouble is often experienced in bringing the machine into powerful action.

When the conductor of the machine is charged with electricity, it acts indirectly on, and accumulates the contrary electricity to its own, at the surface of all the surrounding conductors. It produces the greatest effect on the conductor that is nearest to it and is in the best connection with the ground, whereby the electricity of the same kind as that of the machine may pass to the earth. As the inducing electricity attracts the induced electricity of an opposite kind, so, on the other hand, is the former attracted by the latter. Hence, the electricity which the conductor receives from the machine must especially accumulate at that spot to which another good conductor of electricity is opposed. If a metal disc is in connection with the conductor of a machine, and if another similar disc, which is in good connection with the earth, is placed opposite to it, we have an arrangement by which tolerably large and good conducting surfaces can be brought close to one another: thus the positive condition of the first disc, as well as the negative condition of the other, must be increased to a very considerable degree: the limit is in this case, however, soon reached, because the intervening air easily permits spark-discharge to take place through its substance. With a solid insulating body, as glass or lac, this happens with much greater difficulty, even when the plate of insulating matter is very thin. It is on this principle that instruments for the *accumulation* of electricity depend, among which the Leyden jar is the most important.

Fig. 80.



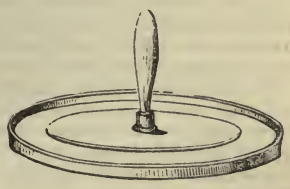
A thin glass jar is coated on both sides with tinfoil, care being taken to leave several inches of the upper part uncovered (fig. 80); a wire, terminating in a metallic knob, communicates with the internal coating. When the outside of the jar is connected with the earth, and the knob put in contact with the conductor of the machine, the inner and outer surfaces of the glass become respectively positive and negative, until a very great degree of intensity has been attained. On completing the connection between the two coatings by a metallic wire or rod, discharge occurs in the form of an exceedingly bright spark, accompanied by a loud snap; and if the human body be interposed in the circuit, the peculiar and disagreeable sensation of the electric shock is felt at the moment of its completion.

By enlarging the dimensions of the jar, or by connecting together a number of such jars in such a manner that all may be charged and discharged simultaneously, the power of the apparatus may be greatly augmented. Thin wires of metal may be fused and dissipated; pieces of wood may be

shattered; many combustible substances set on fire; and all the well-known effects of lightning exhibited upon a small scale.

The electric spark is often very conveniently employed in chemical inquiries for firing gaseous mixtures in closed vessels. A small Leyden jar charged by the machine is the most effective contrivance for this purpose; but, not unfrequently, a method may be resorted to which involves less preparation. The most convenient means of generating electricity is that proposed by Bünsen. A large porcelain tube, which is dry and warm, is wrapped round and rubbed briskly by a dry silken cloth. After each rub the tube is brought in the immediate neighborhood of the knob of a small Leyden jar, the outer coating of this vessel being in connection with the earth. The electrophorus is also frequently used for this purpose. This instrument consists of a round tray or dish of tinned plate, having a stout wire round its upper edge; the width may be about twelve inches, and the depth half an inch. This tray is filled with melted shellac, and the surface rendered as even as possible. A brass disc, with rounded edge, of about nine inches diameter, is also provided, and fitted with an insulating handle. When a spark is wanted, the resinous plate is excited by striking it with a dry, warm piece of fur, or a silk handkerchief; the cover is placed upon it, and touched by the finger, together with the rim of the plate. When the cover is raised, it is found so strongly charged by induction with positive electricity, as to give a bright spark; and, as the resin is not discharged by the cover, which merely touches it at a few points, sparks may be drawn as often as may be wished.

Fig. 81.



It is not known to what cause the disturbance of the electrical equilibrium of the atmosphere is due: experiment has shown that the higher regions of the air are usually in a positive state, the intensity of which reaches a maximum at a particular period of the day. In cloudy and stormy weather the distribution of the atmospheric electricity becomes much deranged, clouds near the surface of the earth often appearing in a negative state.

The circumstances of a thunder-storm exactly resemble those of the charge and discharge of a coated plate or jar; the cloud and the earth represent the two coatings, and the intervening air the bad conducting body or *dielectric*. The polarities of the opposed surface and of the insulating medium between them become raised by mutual induction, until violent disruptive discharge takes place through the air itself, or through any other bodies which may happen to be in the interval. When these are capable of conducting freely, the discharge is silent and harmless; but in other cases it often proves highly destructive. These dangerous effects are now in a great measure obviated by the use of lightning-rods attached to buildings, the erection of which, however, demands a number of precautions not always understood or attended to. The masts of ships may be guarded in like manner by metal conductors: Sir W. Snow Harris has devised a most ingenious plan for the purpose, which is now adopted, with the most complete success, in the Royal Navy.

ELECTRIC CURRENT; ELECTRIC BATTERY.

When two solid conducting bodies are plunged into a liquid which acts upon them unequally, the electric equilibrium is also disturbed, the one acquiring the positive condition, and the other the negative. Thus, pieces

of zinc and platinum put into dilute sulphuric acid, constitute an arrangement capable of generating electrical force: the zinc being the metal attacked, becomes negative; and the platinum remaining unaltered, assumes the positive condition; and on making a metallic communication in any way between the two plates, discharge ensues, as when the two surfaces of a coated and charged jar are put into connection.

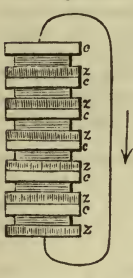
No sooner, however, has this occurred, than the disturbance is repeated; and as these successive charges and discharges take place through the fluid and metals with inconceivable rapidity, the result is an apparently continuous action, to which the term *electrical current* is given.

It is necessary to guard against the idea, which the term naturally suggests, of an actual bodily transfer of something through the substance of the conductors, like water through a pipe: the real nature of all these phenomena is entirely unknown, and may perhaps remain so; the expression is convenient notwithstanding, and consecrated by long use; and with this caution, the very dangerous error of applying figurative language to describe an effect, and then seeking the nature of the effect from the common meaning of words, may be avoided.

The intensity of the electrical excitement developed by a single pair of metals and a liquid is too feeble to affect the most delicate gold-leaf electroscope; but, by arranging a number of such alternations in a connected series, in such a manner that the direction of the current shall be the same in each, the intensity may be very greatly exalted. The two instruments invented by Volta, called the pile and crown of cups, depend upon this principle.

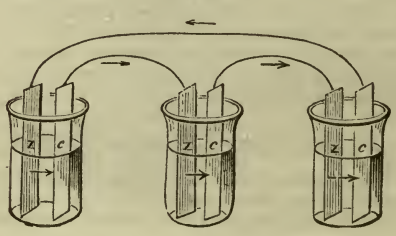
Upon a plate of zinc is laid a piece of cloth, rather smaller than itself, steeped in dilute acid, or any liquid capable of exerting chemical action upon the zinc; upon this is placed a plate of copper, silver, or platinum; then a second piece of zinc, another cloth, and a plate of inactive metal, until a pile of about twenty alternations has been built up. If the two terminal plates be now touched with wet hands, the sensation of the electrical shock will be experienced; but, unlike the momentary effect produced by the discharge of a jar, the sensation can be repeated at will by repeating the contact, and with a pile of one hundred such pairs, excited by dilute acid, it will be nearly insupportable. When such a pile is insulated, the two extremities exhibit strong positive and negative states; and when connection is made between them by wires armed with points of hard charcoal or plumbago, the discharge takes place in the form of a bright enduring spark or stream of fire.

Fig. 82.



The second form of apparatus, or crown of cups, is precisely the same in principle, although different in appearance. A number of cups or

Fig. 83.

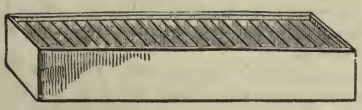


glasses are arranged in a row or circle, each containing a piece of active and a piece of inactive metal, and a portion of exciting liquid — zinc, copper, and dilute sulphuric acid, for example. The copper of the first cup is connected with the zinc of the second, the copper of the second with the zinc of the third, and so to the end of the series. On establishing a communication between the first and last plates by means of a wire, or otherwise, discharge takes place as before.

When any such electrical arrangement consists merely of a single pair of conductors and an interposed liquid, it is called a simple circuit; when two or more alterations are concerned, the term "compound circuit" is applied: they are called also, indifferently, voltaic batteries. In every form of such apparatus, however complex it may appear, the direction of the current may be easily understood and remembered. The polarity or disturbance may be considered to commence at the surface of the metal attacked, and to be propagated through the liquid to the inactive conductor, and thence back again by the connecting wire, these extremities of the battery being always respectively negative and positive when the apparatus is insulated. In common language, it is said that the current in every battery in an active state starts from the metal attacked, passes through the liquid to the second metal or conducting body, and returns by the wire or other channel of communication: hence, in the pile and crown of cups just described, the current *in* the battery is always from the zinc to the copper; and *out* of the battery, from the copper to the zinc, as shown by the arrows.

In the modification of Volta's original pile, made by Mr. Cruikshank, the zinc and copper plates are soldered together and cemented water-tight into a mahogany trough, which thus becomes divided into a series of cells or compartments capable of receiving the exciting liquid. This apparatus is well fitted to exhibit effects of *tension*, to act upon the electroscope, and give shocks: hence its advantageous employment in the application of electricity to medicine, as a very few minutes suffice to prepare it for use.

Fig. 84.



The crown of cups was also put into a much more manageable form by Dr. Babington, and still further improved, as will hereafter be seen, by Dr. Wollaston. Subsequently, various alterations have been made by different experimenters with a view of obviating certain defects in the common batteries, of which a description will be found towards the middle of the volume.

The term "galvanism," sometimes applied to this branch of electrical science, is used in honor of Professor Galvani, of Bologna, who, in 1790, made the very curious observation that convulsions could be produced in the limbs of a dead frog when certain metals were made to touch the nerve and muscle at the same moment. It was Volta, however, who pointed out the electrical origin of these motions; and although the explanation he offered of the source of the electrical disturbance is no longer generally adopted, his name is very properly associated with the invaluable instrument his genius gave to science.

In the year 1822, Professor Seebeck, of Berlin, discovered another source of electricity, to which allusion has already been made — namely, inequality of temperature and conducting power in different metals placed

in contact, or in the same metal in different states of compression and density. Even with a great number of alternations, the current produced is exceedingly feeble compared with that generated by the voltaic pile.

Some animals of the class of fishes, as the *torpedo* or *electric ray*, and the *electric eel* of South America, are furnished with a special organ or apparatus for developing electrical force, which is employed in defence, or in the pursuit of prey. Electricity is here seen to be closely connected with nervous power: the shock is given at the will of the animal, and great exhaustion follows repeated exertion of the power.

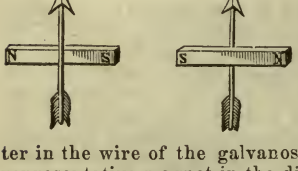
ELECTRO-MAGNETISM; INDUCTION.

Although the fact that electricity is capable, under certain circumstances, both of inducing and of destroying magnetism, has long been known from the effects of lightning on the compass-needle and upon small steel articles, as knives and forks, to which polarity has suddenly been given by the stroke, it was not till 1819 that the laws of these phenomena were discovered by Oersted, of Copenhagen, and shortly afterwards fully developed by Ampère.

The action which a current of electricity, proceeding from any source, exerts upon a magnetized needle, is quite peculiar. The poles or centres of magnetic force are neither attracted nor repelled by the wire carrying the current, but made to move *around* the latter by a force which may be termed *tangential*, and is exerted in a direction perpendicular at once to that of the current, and to the line joining the pole and the wire. Both poles of the magnet being thus acted upon at the same time, and in contrary directions, the needle is forced to arrange itself across the current, so that its axis, or the line joining the poles, may be perpendicular to the wire; and this is always the position which the needle will assume when the influence of terrestrial magnetism is in any way removed. This curious angular motion may even be shown by suspending a magnet in such a way that only one of its poles shall be subjected to the current; a permanent movement of rotation will continue as long as the current is kept up, its direction being changed by altering the pole, or reversing the current. The movable connections are made by mercury, into which the points of the conducting wires dip.

It is often of great practical consequence to be able to predict the direction in which a particular pole shall move by a given current, because in all galvanoscopes and other instruments involving these principles, the movement of the needle is taken as an indication of the direction of the circulating current. And this is easily done by a simple mechanical aid to the memory: Let the current be supposed to pass through a watch from the face to the back; the motion of the north pole will be in the direction of the hands. Or a little piece of apparatus may be used if reference is often required: this is a piece of pasteboard, or other suitable material, cut into the form of an arrow for indicating the current, crossed by a magnet having its poles marked, and arranged in the true position with respect to the current. The direction of the latter in the wire of the galvanoscope can at once be known by placing the representative magnet in the direction assumed by the needle itself.

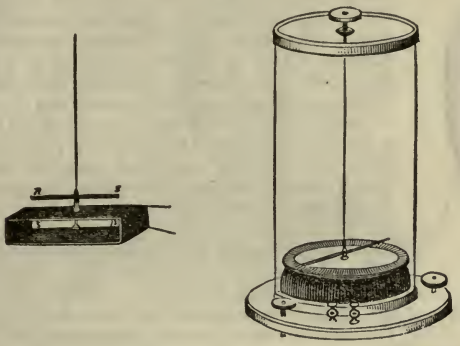
Fig. 85.



The common galvanoscope (fig. 86), consisting of a coil of wire having a compass-needle suspended on a point within it, is greatly improved by the addition of a second needle, as already in part described (p. 102), and by

a better mode of suspension, a long fibre of silk being used for the purpose. The two needles are of equal size, and magnetized as nearly as possible to the same extent; they are then immovably fixed together parallel, and

Fig. 86.

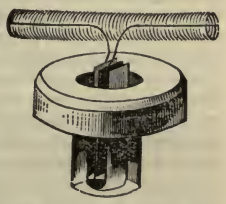


with their poles opposed, and hung with the lower needle in the coil and the upper one above it. The advantage gained is twofold: the system is *astatic*, unaffected, or nearly so, by the magnetism of the earth; and the needles, being both acted upon in the same manner by the current, are urged with much greater force than one alone would be, all the actions of every part of the coil being strictly concurrent. A divided circle is placed below the upper needle, by which the angular motion can be measured; and the whole is enclosed in glass, to shield the needles from the agitation of the air. The whole is shown in fig. 86.

The action between the pole and the wire is mutual, as may be shown by rendering the wire itself movable, and placing a magnet in its vicinity: on completing the circuit, the wire will be put in motion, and, if the arrangement permits, it will rotate around the magnetic pole.

A little consideration will show that, from the peculiar nature of the electro-dynamic force, a wire carrying a current, bent into a spiral or helix, must possess the properties of an ordinary magnetized bar, its extremities being attracted and repelled by the poles of a magnet. Such is really found to be the case, as may be proved by a variety of arrangements, among which it will be sufficient to cite the beautiful little apparatus of Professor de la Rive. A short wide glass tube is fixed into a cork ring of considerable size (fig. 87); a little voltaic battery, consisting of a single pair of copper and zinc plates, is fitted to the tube, and to these the ends of the spiral are soldered. On filling the tube with dilute acid, and floating the whole in a large basin of water, the helix will be observed to arrange itself in the magnetic meridian, and on trial it will be found to obey a magnet held near it in the most perfect manner, as long as the current circulates.

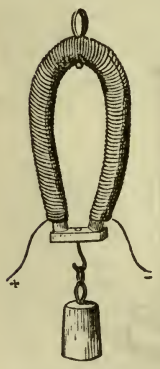
Fig. 87.



When an electric current is passed at right angles to a piece of iron or steel, the latter acquires magnetic polarity, either temporary or permanent, as the case may be, the direction of the current determining the position

of the poles. This effect is prodigiously increased by causing the current to circulate a number of times round the bar, which then acquires extraordinary magnetic power. A piece of soft iron, worked into the form of a horse-shoe (fig. 88), and surrounded by a coil of copper wire covered with silk or cotton for the purpose of insulation, furnishes an excellent illustration of the inductive energy of the current in this respect: when the ends of the wire are put into communication with a small voltaic battery of a single pair of plates, the iron instantly becomes so highly magnetic as to be capable of sustaining a very heavy weight.

Fig. 88.



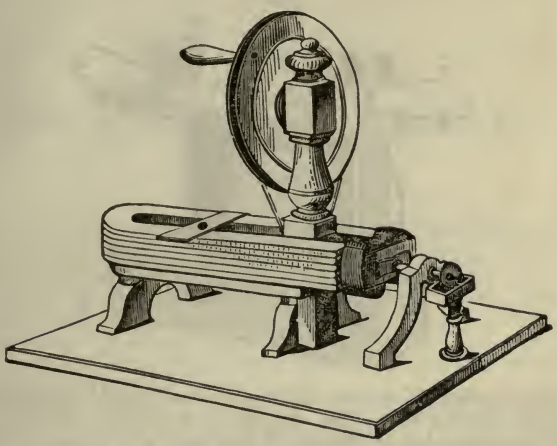
Ampère discovered, in the course of his investigations, a number of extremely interesting phenomena resulting from the action of electrical currents on each other, which become evident when arrangements are made for giving mobility to the conducting wires. He found that when two currents, flowing in the same direction, are made to approach each other, strong attraction takes place between them, and, when in opposite directions, an equally strong repulsion. These effects, which are not difficult to demonstrate, have absolutely no relation, that can be traced, to ordinary electrical attractions and repulsions, from which they must be carefully distinguished; they are purely *dynamic*, having to do with electricity in motion. Ampère founded upon this discovery a most beautiful and ingenious hypothesis of magnetic actions in general, which explains very clearly the influence of the current upon the needle.

A current of electricity can thus develop magnetism in a transverse direction to its own; in the same manner, magnetism can call into activity electric currents. If the two extremities of the coil of the electro-magnet above described be connected with a galvanoscope, and the iron magnetized by the application of a permanent steel horse-shoe magnet to the ends of the bar, a momentary current will be developed in the wire, and pointed out by the movement of the needle. It lasts but a single instant, the needle returning after a few oscillations to a state of rest. On removing the magnet, whereby the polarity of the iron is at once destroyed, a second current or wave will become apparent, but in the opposite direction to that of the first. By employing a very powerful steel magnet, surrounding its iron keeper or armature with a very long coil of wire, and then making the armature itself rotate in front of the faces of the magnet, so that its induced polarity shall be rapidly reversed, magneto-electric currents may be produced, of such intensity as to give bright sparks and most powerful shocks, and exhibit all the phenomena of voltaic electricity. Fig. 89 represents a very powerful arrangement of this kind.

When two covered wires are twisted together or laid side by side for some distance, and a current transmitted through the one, a momentary electrical wave will be induced in the other in the reverse direction; and on breaking connection with the battery, a second single wave will become evident by the aid of the galvanoscope, in the same direction as that of the primary current. In the same way, when a current of electricity passes through one turn in a coil of wire, it induces two secondary currents in all the other turns of the coil; when the circuit is closed, the first is moving in the opposite direction to the primary current; the second, when the circuit is broken, has a motion in the same direction as the primary current. The effect of the latter is added to that of the primary current. Hence, if a wire coil be made part of the conducting wire of a weak electric pile, and if the primary current, by means of an appropriate arrangement,

be made and broken in rapid succession, we can increase in a remarkable manner the effects which are produced at the moment of breaking the cir-

Fig. 89.

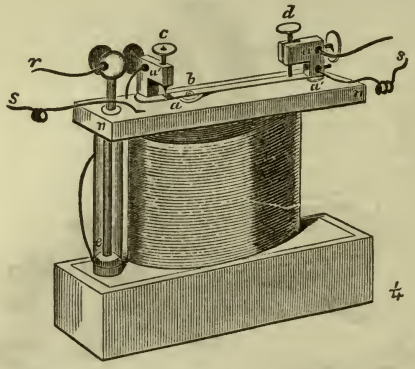


cuit either at the place of interruption, such as the spark-discharges, or in secondary closing conductors, as in the action on the nerves or the decomposition of water.

If two copper wires, the one above the other, be twisted round the same hollow cylinder, and one of these wires — for instance, the inner one — be made part of a galvanic circuit, a current of short duration is induced in the outer wire, both by making and by breaking contact. The strength of this current can be very appreciably increased by filling the hollow cylinder with a bundle of thin iron rods, when magnetic and electrical induction are made to co-operate. The more frequently contact is alternately made and broken, the greater is the number of induced currents that follow each other, and the more powerful, within certain limits, is the action. Dr. Neef has constructed an ingenious contrivance, in which contact is made and broken by the current itself, whereby his induction apparatus actually becomes an electrical machine. Fig. 90 exhibits the original apparatus slightly modified. The arrangement consists essentially of an elastic copper strip $a\ a'$, which is fixed at a', and carries at b a small plate of soft iron. The latter hangs over the iron rods of the induction coil, which are somewhat raised in this particular point, but without touching them. The end, a, of the copper strip is covered with a little plate of platinum, which presses against a platinum point of the screw c. The current, having traversed the inner coil, passes from the point c, to the plate a, in order to return through the copper strip $a\ a'$, and the wire s'. By the passage of the current the iron rods have become magnetic and attract the iron plate, b, whereby the end, a, of the copper strip is removed from the platinum point, and contact is broken. But as soon as the current ceases, the iron rods lose their magnetism, the elastic copper strip returns to its former position, and establishes again the current for a short time. The screws, c and d, regulate the position of the spring and the time of its oscillations, the velocity of which may be estimated by the pitch of the notes produced. This apparatus, which was first made by Dr. Neef, in 1830, has been con-

siderably improved within the last few years. Ruhmkorff especially, by a more perfect isolation of the wire coils, has succeeded to a much greater extent in preserving the electrical induction. He has thus obtained a state

Fig. 90.



of electrical tension which resembles that produced by frictional electricity; the spark is capable of crossing the air in measurable distances, not in isolated discharges, but in streams of brilliant light. The shocks of this apparatus resemble those of a moderate Leyden jar, but differ from the latter by the rapidity with which they may be repeated at pleasure. By means of Ruhmkorff's coil, Grove has lately effected decompositions in water and other bad conducting liquids, which resemble those obtained many years ago by Wollaston by means of the electrical machine. Those phenomena of decomposition, which in water, for instance, furnish oxygen and hydrogen at the same pole, must be distinguished from true electrical decompositions; they are, in fact, effects of heat, as Grove has pointed out.

ELECTRICITY OF VAPOR.

The electricity exhibited under certain peculiar circumstances by a jet of steam, first observed by mere accident, but since closely investigated by Sir W. Armstrong, and also by Faraday, is now referred to the friction, not of the pure steam itself, but of particles of condensed water, against the interior of the exit-tube. It has been proved with certainty in the last few years that evaporation alone is not capable of disturbing the electrical equilibrium, and the hope first entertained, that these phenomena would throw light upon the cause of electrical excitement in the atmosphere, is now abandoned. The steam is usually positive, if the jet-pipe be constructed of wood or clean metal, but the introduction of the smallest trace of oily matter causes a change of sign. The intensity of the charge is, *cæteris paribus*, increased with the elastic force of the steam. By this means effects have been obtained very far surpassing those of the most powerful plate electrical machines ever constructed.

Although no electricity can be directly evolved by evaporation, yet vapor possesses in a high degree the property of discharging into the atmosphere that electricity which often accumulates in bodies from which it arises. The fresh branches and leaves of trees do this to the greatest extent. When moistened with rain or dew, their surfaces become positively electrical, whilst the internal parts, even to the roots, become negatively electrical.

PART II.

CHEMISTRY OF ELEMENTARY BODIES.

THE term *element* or *elementary substance* is applied in chemistry to those forms of modifications of matter which have hitherto resisted all attempts to decompose them. Nothing is ever meant to be affirmed concerning their real nature; they are simply elements to us at the present time; hereafter, by new methods of research, or by new combinations of those already possessed by science, many of the substances which now figure as elements may possibly be shown to be compounds; this has already happened, and may again take place.

The elementary bodies, at present recognized, amount to sixty-four in number; of these, about fifty belong to the class of *metals*. Several of these are of recent discovery, and as yet very imperfectly known. The distinction between metals and non-metallic substances, or *metalloïds*, although very convenient for purposes of description, is entirely arbitrary, since the two classes graduate into each other in the most complete manner.

It will be proper to commence with the latter and less numerous division. The elements are named as in the subjoined table, the most important being distinguished by the largest and most conspicuous type, those next in importance by medium type, whilst the names of elements which are either of rare occurrence, or of which our knowledge is very imperfect, are printed in the smallest type.

METALLOÏDS.	METALS.		
Boron.	**ALUMINIUM.**	Iridium.	Ruthenium.
BROMINE.	Antimony.	**IRON.**	**SILVER.**
CARBON.	Arsenic.	Lanthanum.	**SODIUM.**
CHLORINE.	Barium.	**LEAD.**	Strontium.
FLUORINE.	Beryllium.	Lithium.	Tantalum.
HYDROGEN.	Bismuth.	Magnesium.	Terbium.
IODINE.	Cadmium.	**MANGANESE.**	Thallium.
NITROGEN.	Cæsium.	**MERCURY.**	Thorinum.
OXYGEN.	**CALCIUM.**	Molybdenum.	**TIN.**
PHOSPHORUS.	Cerium.	Nickel.	Titanium.
Selenium.	Chromium.	Niobium.	Tungsten.
SILICIUM.	Cobalt.	Osmium.	Uranium.
SULPHUR.	**COPPER.**	Palladium.	Vanadium.
Tellurium.	Didymium.	Platinum.	Yttrium.
	Erbium.	**POTASSIUM.**	**ZINC.**
	Gold.	Rhodium.	Zirconium.
	Indium.	Rubidium.	

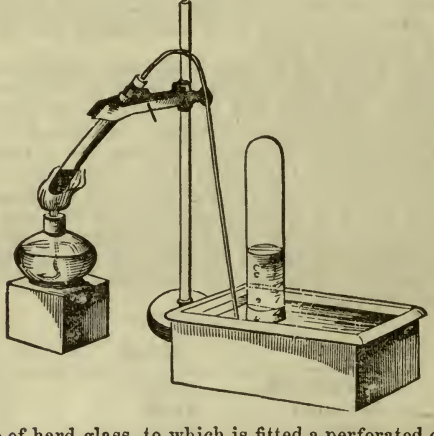
OXYGEN.

Whatever plan of classification, founded on the natural relations of the elements, be adopted, it will always be found most advantageous, in the practical study of chemistry, to commence with the consideration of the great constituents of the ocean and the atmosphere.

Oxygen was discovered in the year 1774, by Scheele, in Sweden, and Dr. Priestley, in England, independently of each other, and described under the terms *empyreal air* and *dephlogisticated air*. The name oxygen* was given to it by Lavoisier some time afterward. Oxygen exists in a free and uncombined state in the atmosphere, mingled with another gaseous body, nitrogen. No very good direct means exist, however, for separating it from the latter; and, accordingly, it is always obtained for purposes of experiment by decomposing certain of its compounds, which are very numerous.

The red oxide of mercury, or *red precipitate* of the old writers, may be employed with this view. In this substance the attraction which holds together the mercury and the oxygen is so feeble, that simple exposure to heat suffices to bring about decomposition. The red precipitate is placed

Fig. 91.



in a short tube of hard glass, to which is fitted a perforated cork, furnished with a piece of narrow glass tube, bent as in fig. 91. The heat of a spirit-lamp being applied to the substance, decomposition speedily commences; globules of metallic mercury collect in the cool part of the wide tube, which answers the purpose of a retort, while gas issues in considerable quantity from the apparatus. This gas is collected and examined by the aid of the pneumatic trough, which consists of a vessel of water provided with a shelf, upon which stand the jars or bottles destined to receive the gas, filled with water and inverted. By keeping the level of the liquid above the mouth of the jar, the water is retained in the latter by the pressure of the atmosphere, and entrance of air is prevented. When the jar is brought over the extremity of the gas-delivering tube, the bubbles of gas rising through the water, collect in the upper part of the jar, and displace the liquid. As soon as one jar is filled, it may be removed, still keeping its mouth below the water-level, and another substituted. The whole arrangement is shown in fig. 91.

* From ὀξὺς, acid, and γεν, a root signifying production.

The experiment here described is more instructive as an excellent case of the resolution by simple means of a compound body into its constituents,* than valuable as a source of oxygen gas. A better and more economical method is to expose to heat in a retort, or flask furnished with a bent tube, a portion of the salt called potassium chlorate. A common Florence flask serves perfectly well, the heat of a spirit-lamp being sufficient. The salt melts and decomposes with ebullition, yielding a very large quantity of oxygen gas, which may be collected in the way above described. The first portion of the gas often contains a little chlorine. The white saline residue in the flask is potassium chloride. This plan, which is very easy of execution, is always adopted when very pure gas is required for analytical purposes.†

A third method, very good when perfect purity is not demanded, is to heat to redness, in an iron retort or gun-barrel, the black manganese oxide of commerce, which under these circumstances suffers decomposition, although not to the extent manifest in the red precipitate.‡

If a little of the black manganese oxide be finely powdered and mixed with potassium chlorate, and the mixture heated in a flask or retort by a lamp, oxygen will be disengaged with the utmost facility, and at a far lower temperature than when the chlorate alone is used.§ All the oxygen comes from the chlorate, the manganese remaining quite unaltered. The materials should be well dried in a capsule before their introduction into the flask. This experiment affords an instance of an effect by no means rare, in which a body seems to act by its mere presence, without taking any obvious part in the change brought about.

Methods for the preparation of oxygen on a large scale will be found described under the heads of sulphuric acid and barium dioxide.

Whatever method be chosen — and the same remark applies to the collection of all other gases by similar means — the first portions of gas must be suffered to escape, or be received apart, as they are contaminated by the atmospheric air of the apparatus. The practical management of gases is a point of great importance to the chemical student, and one with which he must endeavor to familiarize himself. The water-trough just described is one of the most indispensable articles of the laboratory, and by its aid all experiments on gases are carried on when the gases themselves are not sensibly acted upon by water. The trough is best constructed of japanned copper, the form and dimensions being regulated by the magnitude of the jars. It should have a firm shelf, so arranged as to be always about an inch below the level of the water, and in the shelf a groove should be made about half an inch in width, and the same in depth, to admit the extremity

* Chemists are in the habit of representing the elements by symbols, and their compounds by formulæ. The same symbolical language, which is fully explained in a subsequent section of the work (General Principles of Chemical Philosophy), is used for representing the changes which the chemical compounds undergo. For the benefit of the advanced student, the formulæ expressing the more important decompositions are now given in foot-notes. The decomposition of mercuric oxide is thus represented: —

$$\overbrace{HgO}^{\text{Mercuric oxide.}} = \overbrace{Hg}^{\text{Mercury.}} + \overbrace{O}^{\text{Oxygen.}}$$

† $$\overbrace{KClO_3}^{\text{Potassium chlorate.}} = \overbrace{KCl}^{\text{Potassium chloride.}} + \overbrace{O_3}^{\text{Oxygen.}}$$

‡ $$\overbrace{3MnO_2}^{\text{Manganese dioxide.}} = \overbrace{Mn_3O_4}^{\text{Manganoso-manganic oxide.}} + \overbrace{O_2}^{\text{Oxygen.}}$$

§ [The manganese oxide should not contain any combustible matter, or an explosion will result. Accidents have occurred from this cause, and a preliminary trial should be made by heating a small quantity in a metal cup, should there be any doubt of the purity of the oxide. — R. B.]

of the delivery-tube beneath the jar, which stands securely upon the shelf. When the pneumatic trough is required of tolerably large dimensions, it may with great advantage have the form and disposition represented in

Fig. 92.

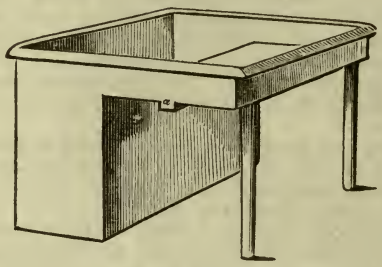
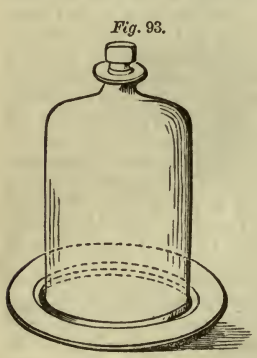


fig. 92. The end of the groove spoken of, which crosses the shelf or shallow portion, is shown at *a*.

Gases are transferred from jar to jar with the utmost facility, by first filling the vessel, into which the gas is to be passed with water, inverting it, carefully retaining its mouth below the water-level, and then bringing beneath it the aperture of the jar containing the gas. On gently inclining the latter, the gas passes by a kind of inverted decantation into the second vessel. When the latter is narrow, a funnel may be placed loosely in its neck, by which loss of gas will be prevented.

Fig. 93.



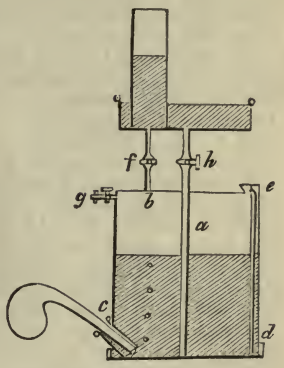
A jar wholly or partially filled with gas at the pneumatic trough may be removed by placing beneath it a shallow basin, or even a common plate, so as to carry away enough water to cover the edge of the jar: and many gases, especially oxygen, may be so preserved for many hours without material injury.

Gas-jars are often capped at the top, and fitted with a stop-cock for transferring gas to bladders or caoutchouc bags. When such a vessel is to be filled with water, it may be slowly sunk in an upright position in the well of the pneumatic trough, the stop-cock being open to allow the air to escape, until the water reaches the brass cap. The cock is then to be turned, and the jar lifted upon the shelf, and filled with gas in the usual way. If the trough be not deep enough for this method of proceeding, the mouth may be applied to the stop-cock, and the vessel filled by sucking out the air until the water rises to the cap. In all cases it is proper to avoid as much as possible wetting the stop-cocks and other brass apparatus.

Mr. Pepys contrived, many years ago, an admirable piece of apparatus for storing and retaining large quantities of gas. It consists of a drum or reservoir of sheet copper, surmounted by a shallow trough or cistern, the communication between the two being made by a couple of tubes, *a b*, furnished with stop-cocks, one of which, *h f*, passes nearly to the bottom of the drum, as shown in fig. 94. A short wide open tube, *c*, is inserted obliquely near the bottom of the vessel, into which a plug may be tightly screwed.

A stop-cock, *g*, near the top, serves to transfer gas to a bladder or tube-apparatus. A glass water-gauge, *d e*, affixed to the side of the drum, and communicated with both top and bottom, indicates the level of the liquid within.

Fig. 94.



To use the gas-holder, the plug is first screwed into the lower opening, and the drum completely filled with water. All three stop-cocks are then to be closed and the plug removed. The pressure of the atmosphere retains the water in the gas-holder, and if no air-leakage occurs, the escape of water is inconsiderable. The extremity of the delivery-tube is now to be well pushed through the open aperture into the drum, so that the bubbles of gas may rise without hindrance to the upper part, displacing the water, which flows out in the same proportion into a vessel placed for its reception. When the drum is filled, or enough gas has been collected, the tube is withdrawn and the plug screwed into its place.

When a portion of the gas is to be transferred to a jar, the latter is to be filled with water at the pneumatic trough, carried by the help of a basin or plate to the cistern of the gas-holder, and placed over the shorter tube. On opening the cock of the neighboring tube, the hydrostatic pressure of the column of water will cause compression of the gas, and increase its elastic force, so that, on gently turning the cock beneath the jar, it will ascend into the latter in a rapid stream of bubbles. The jar, when filled, may again have the plate slipped beneath it, and be removed without difficulty.

Oxygen, when free or uncombined, is known only in the gaseous state, all attempts to reduce it to the liquid or solid condition by cold and pressure having completely failed. When pure, it is colorless, tasteless, and inodorous. It is the sustaining principle of animal life, and of all the ordinary phenomena of combustion.

Bodies which burn in the air, burn with greatly increased splendor in oxygen gas. If a taper be blown out, and then introduced while the wick remains red-hot, it is instantly rekindled: a slip of wood or a match is relighted in the same manner. This effect is highly characteristic of oxygen, there being but one other gas which possesses the same property; and this is easily distinguished by other means. The experiment with the match is also constantly used as a rude test of the purity of the gas when it is about to be collected from the retort, or when it has stood some time in contact with water exposed to air.

When a bit of charcoal is affixed to a wire, and plunged with a single point red-hot into a jar of oxygen, it burns with great brilliancy, throwing off beautiful scintillations, until, if the oxygen be in excess, it is completely consumed. An iron wire, or, still better, a steel watch-spring, armed at its extremity with a bit of lighted amadou, and introduced into a vessel of oxygen gas, exhibits a most beautiful phenomenon of combustion. If the experiment be made in a jar standing on a plate, the fused globules of black iron oxide fix themselves in the glaze of the latter, after falling through a stratum of water half an inch in depth. Kindled sulphur burns with great beauty in oxygen; and phosphorus, under similar circumstances, exhibits a splendor which the eye is unable to support.

In these and many other similar cases which might be mentioned, the

same ultimate effect is produced as in atmospheric air; the action is, however, more energetic, from the absence of the gas which, in the air, dilutes the oxygen and enfeebles its chemical powers. The process of respiration in animals is an effect of the same nature as common combustion. The blood contains substances which slowly burn by the aid of the oxygen thus introduced into the system. When this action ceases, life becomes extinct.

Oxygen is bulk for bulk a little heavier than atmospheric air, its specific gravity being 1·10563, referred to that of air as unity, and 16 referred to that of hydrogen as unity. A litre of oxygen at the standard temperature and pressure, that is to say, at 0° C., and 760 millimetres barometric pressure, weighs 1·43028 gram. At 15·5° C. (60° F.), and under a pressure of 30 inches, 100 cubic inches of the gas weigh 34·29 grains.*

It has been already remarked, that to determine with the utmost degree of accuracy the specific gravity of a gas, is an operation of very great practical difficulty, but at the same time of very great importance. There are several methods which may be adopted for this purpose: the one described below appears, on the whole, to be the simplest and best. It requires, however, the most scrupulous care, and the observance of a number of minute precautions which are absolutely indispensable to success.

The plan of the operation is as follows: A large glass globe is to be filled with the gas to be examined in a perfectly pure and dry state, having a known temperature, and an elastic force equal to that of the atmosphere at the time of the experiment. The globe so filled is to be weighed. It is then to be exhausted at the air-pump as far as possible, and again weighed. Lastly, it is to be filled with dry air, the temperature and pressure of which are known, and its weight once more determined. On the supposition that the temperature and elasticity are the same in both cases, the specific gravity is at once obtained by dividing the weight of the gas by that of the air.

The globe or flask must be made very thin, and fitted with a brass cap, surmounted by a small but excellent stop-cock. A delicate thermometer should be placed in the inside of the globe, secured to the cap. The gas must be generated at the moment, and conducted at once into the previously exhausted vessel, through a long tube filled with fragments of pumice moistened with oil of vitriol, or some other extremely hygroscopic substance, by which it is freed from all moisture. As the gas is necessarily generated under some pressure, the elasticity of that contained in the filled globe will slightly exceed the pressure of the atmosphere; and this is an advantage, since, by opening the stop-cock for a single instant, when the globe has attained an equilibrium of temperature, the tension becomes exactly that of the air, so that all barometrical correction is avoided, unless the pressure of the atmosphere should sensibly vary during the time occupied by the experiment. It is hardly necessary to remark that the greatest care must also be taken to purify and dry the air used as the standard of comparison, and to bring both gas and air as nearly as possible to the same temperature, to obviate the necessity of a correction, or at least to diminish almost to nothing the errors involved by such a process.

Oxides. — The compounds formed by the direct union of oxygen with other bodies bear the general name of oxides: these are very numerous and important. They are conveniently divided into three principal groups or classes. The first division contains all those oxides which resemble in their chemical relations the oxides of potassium, sodium, silver, or lead: these are denominated *alkaline* or *basic oxides*. The oxides of the second group have properties opposed to those of the bodies mentioned; the oxides

* Dumas, Ann. Chim. Phys. [3], iii. 275.

of sulphur and phosphorus may be taken as the typical representatives of the class: they are called *acid oxides*, and are capable of uniting with the basic oxides, and forming compounds called *salts*. Thus, when the oxide of sulphur, called sulphuric oxide, is passed in the state of vapor over heated barium oxide, combination takes place, attended with vivid incandescence, and a salt called barium sulphate is produced, containing all the elements of the two original bodies, namely, barium, sulphur, and oxygen.

There is also an intermediate group of oxides called *neutral oxides*, from their slight disposition to enter into combination. The black oxide of manganese, already mentioned, is an excellent example. It must not be supposed, however, that the three groups of oxides just mentioned are separated from each other by decided lines of demarcation; on the contrary, they blend into one another by imperceptible degrees, and the same oxide may, in many cases, exhibit either acid or basic relations according to the circumstances under which it is placed.

Among salts, there is a particular group, namely, the *hydrogen salts*, containing the elements of an acid oxide, and water (hydrogen oxide), which are especially distinguished as *acids*, because many of them possess in an eminent degree the properties to which the term acid is generally applied, such as a sour taste, corrosive action, solubility in water, and the power of reddening certain blue vegetable colors. A characteristic property of these acids, or hydrogen salts, is their power of exchanging their hydrogen for a metal presented to them in the free state, or in the form of oxide. Thus, sulphuric acid, which contains sulphur, oxygen, and hydrogen, readily dissolves metallic zinc, the metal taking the place of the hydrogen, which is evolved as gas, and forming a salt containing sulphur, oxygen, and zinc; in fact, a *zinc sulphate*, produced from a *hydrogen sulphate* by substitution of zinc for hydrogen.* The same substitution and formation of zinc sulphate take place when zinc oxide is brought in contact with sulphuric acid; but in this case the hydrogen, instead of being evolved as gas, remains combined with the oxygen derived from the zinc oxide, forming water.†

A series of oxides containing quantities of oxygen in the proportion of the numbers 1, 2, 3, united with a constant quantity of another element, are distinguished as *monoxide*, *dioxide*, and *trioxide* respectively, the Greek numerals indicating the several degrees of oxidation. A compound intermediate between a monoxide and a dioxide is called a *sesquioxide*, *e. g.*:

	Chromium.		Oxygen.
Chromium monoxide	52·5	+	16
Chromium sesquioxide	52·5	+	24
Chromium dioxide	52·5	+	32
Chromium trioxide	52·5	+	48

When a metal forms two basic or salifiable oxides, they are distinguished by adjectival terms ending in *ous* for the lower, and *ic* for the higher degree of oxidation, *e. g.*:

	Iron.		Oxygen.
Iron monoxide, or Ferrous oxide	56	+	16
Iron sesquioxide, or Ferric oxide	56	+	24

The salts resulting from the action of acids on these oxides are also distinguished as ferrous and ferric salts respectively.

Acid oxides of the same element, sulphur for example, are also distinguished by the terminations *ous* and *ic*, applied as above; their acids,

* $SO_4H_2 + Zn = SO_4Zn + H_2$

12

† $SO_4H_2 + Zn\,O = SO_4Zn + OH_2$

or hydrogen salts, receive corresponding names; and the salts formed from these acids are distinguished by names ending in *ite* and *ate* respectively. Thus, for the oxides and salts of sulphur:

	Sulphur.		Oxygen.		
Sulphurous oxide	32	+	32		
					Hydrogen.
Hydrogen sulphite, or Sulphurous acid	32	+	48	+	2
					Lead.
Lead sulphite	32	+	48	+	207
Sulphuric oxide	32	+	48		
					Hydrogen.
Hydrogen sulphate, or Sulphuric acid	32	+	64	+	2
					Lead.
Lead sulphate	32	+	64	+	207

The acids above spoken of are oxygen-acids; and formerly it was supposed that all acids contained oxygen — that element being, indeed, regarded as the acidifying principle; hence its name (p. 128). At present, however, we are acquainted with many bodies which possess all the characters above specified as belonging to an acid, and yet do not contain oxygen. For example, hydrochloric acid (formerly called muriatic acid, or spirit of salt) — which is a hydrogen chloride, or compound of hydrogen and chlorine — is intensely sour and corrosive; reddens litmus strongly; dissolves zinc, which drives out the hydrogen and takes its place in combination with the chlorine, forming zinc-chloride; and dissolves most metallic oxides, exchanging its hydrogen for the metal, and forming a metallic chloride and water.*

Bromine, iodine, and fluorine also form, with hydrogen, acid compounds analogous in every respect to hydrochloric acid.

Compounds of chlorine, bromine, iodine, fluorine, sulphur, selenium, phosphorus, &c., with hydrogen and metals, are grouped, like the oxygen compounds, by names ending in *ide:* thus we speak of zinc chloride, calcium fluoride, hydrogen sulphide, copper phosphide, &c. The numerical prefixes, *mono, di, tri,* &c., as also the terminations *ous* and *ic,* are applied to these compounds in the same manner as to the oxides, thus:

	Hydrogen.		Bromine.
Hydrogen bromide	1	+	80
	Potassium.		Sulphur.
Potassium monosulphide	78·2	+	32
Potassium disulphide	78·2	+	64
Potassium trisulphide	78·2	+	96
Potassium tetrasulphide	78·2	+	128
Potassium pentasulphide	78·2	+	160
	Iron.		Chlorine.
Ferrous chloride	56	+	71
Ferric chloride	56	+	105·5
	Tin.		Sulphur.
Stannous sulphide	118	+	64
Stannic sulphide	118	+	128

The Latin prefixes *uni, bi, ter, quadro,* &c., are often used instead of the corresponding Greek prefixes; there is no very exact rule respecting their

* Action of hydrochloric acid on zinc:
$2HCl + Zn = ZnCl_2 + H_2$
Action of hydrochloric acid on zinc oxide:
$2HCl + ZnO = ZnCl_2 + OH_2$

use: but, generally speaking, it is best to employ a Greek or Latin prefix, according as the word before which it is placed is of Greek or Latin origin; thus, *di*oxide corresponds to *bi*sulphide; on the whole, however, the Greek prefixes are most generally employed.

Ozone. — It has long been known that dry oxygen, or atmospheric air, when exposed to the action of a series of electric sparks, emits a peculiar and somewhat metallic odor. The same odor may be imparted to moist oxygen by allowing phosphorus to remain for some time in it, and by several other processes. A more accurate examination of this odorous air has shown that, in addition to the smell, it possesses several properties not exhibited by oxygen in its ordinary state. One of its most characteristic effects is the liberation of iodine from potassium iodide. This odorous principle has been the subject of many researches, in particular by Schönbein, of Basle, who proposed for it the name of *ozone*.*

An easy method of exhibiting the production of ozone is to transmit a current of oxygen through a tube into which a pair of platinum wires is sealed, with the points at a little distance apart; on connecting one of the wires with the prime conductor of an electrical machine in good action, and the other with the ground, the characteristic odor of ozone is immediately developed in the issuing gas; but, notwithstanding the powerful odor thus produced, only a small portion of the oxygen undergoes this change. Andrews and Tait have shown that, to obtain the maximum of ozone, it is necessary to transmit the discharge silently, between very fine points; if sparks are allowed to pass, a considerable portion of the ozone is reconverted into ordinary oxygen as fast as it is formed. Siemens prepares ozone by induction: he forms a sort of Leyden jar, by coating the interior of a long tube with tin-foil, and passes over this tube a second wider tube coated with tin-foil on its outer surface. Between the two tubes a current of pure dry oxygen is passed, which becomes electrified by induction, on connecting the inner and outer coating with the terminal wires of an induction-coil; by this means it is said that from 10 to 15 per cent. of the oxygen may be converted into ozone.

Ozone may also be obtained in several ways, without the aid of electricity; thus it is formed in small quantity when a stick of phosphorus is suspended in a bottle filled with moist air; by the slow oxidation of ether, oil of turpentine, and other essential oils; in the electrolytic decomposition of water; and by the action of strong sulphuric acid on potassium permanganate.† There has been considerable discussion about the nature and composition of ozone; but the most trustworthy experiments seem to show that, in whatever way produced, it is merely a modified form of oxygen.

Ozone is insoluble in water and in solutions of acids or alkalies, but is absorbed by a solution of potassium iodide. Air charged with it exerts an irritating action on the lungs. Ozone is decomposed by heat, gradually at 100° C. (212° F.,) instantly at 290° C. (554° F.) It is an extremely powerful oxidizing agent; possesses strong bleaching and disinfecting powers; corrodes cork, caoutchouc, and other organic substances; and rapidly oxidizes iron, copper, and even silver when moist, as well as dry mercury and iodine. It is remarkable that the absorption of ozone by these and other agents is not attended with any contraction of volume. The explanation of this fact appears to be, that oxygen when ozonized diminishes in volume (in the proportion of 3 to 2, according to Soret), and that when the ozone is decomposed by a metal or other substance, one portion of it enters into combination, while the remainder, which is set free as ordinary oxygen, occupies the same bulk as the ozone itself.

* From ὄζειν, to emit an odor.

[† Also, according to A. Houseau, by the action of sulphuric acid on barium dioxide. — R. B.]

The most delicate test for the presence of ozone in any gas is afforded by a strip of paper moistened with a mixture of starch and solution of potassium iodide. On exposing such paper to the action of ozone, the potassium iodide is decomposed, its potassium combining with oxygen, while the iodine is liberated, and forms a deep blue compound with the starch. Now, when paper thus prepared is exposed to the open air for five or ten minutes, it often acquires a blue tint, the intensity of which varies on different days. Hence it has been plausibly supposed that ozone is present in the air in variable quantity. But iodine may be liberated from potassium iodide by many other agents, especially by certain oxides of nitrogen, which are very likely to be present in the air in minute quantities: hence the existence of ozone in the air cannot be proved to be present by this reaction alone.

HYDROGEN.

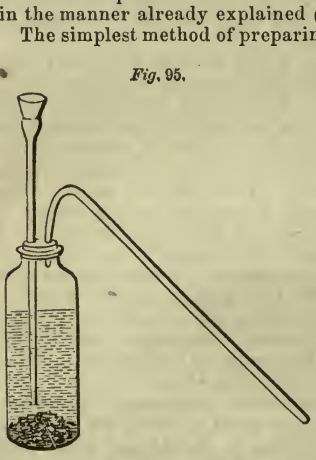
Hydrogen may be obtained for experimental purposes by deoxidizing water, of which it forms a characteristic component.*

If a tube of iron or porcelain, containing a quantity of filings or turnings of iron, be fixed across a furnace, and its middle portion be made red-hot, and then the vapor of water transmitted over the heated metal, a large quantity of permanent gas will be disengaged from the tube, and the iron will become converted into oxide, and acquire an increase in weight. The gas is hydrogen: it may be collected over water and examined.

Hydrogen is, however, more easily obtained by decomposing hydrochloric or dilute sulphuric acid with zinc, the metal then displacing the hydrogen in the manner already explained (p. 133).

The simplest method of preparing the gas is the following: A wide-necked bottle is chosen, and fitted with a sound cork, perforated by two holes for the reception of a small tube-funnel reaching nearly to the bottom of the bottle, and a piece of bent glass tube to convey away the disengaged gas. Granulated zinc, or scraps of the malleable metal, are put into the bottle, together with a little water, and sulphuric acid slowly added by the funnel, the point of which should dip into the liquid. The evolution of gas is easily regulated by the supply of acid; and when enough has been discharged to expel the air of the vessel, it may be collected over water in a jar, or passed into a gas-holder. In the absence of zinc, filings of iron or small nails may be used, but with less advantage.

Fig. 95.



A little practice will soon enable the pupil to construct and arrange a variety of useful forms of apparatus, in which bottles, and other articles always at hand, are made to supersede more costly instruments. Glass tube, purchased by weight of the maker,

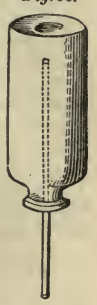
* Hence the name, from ὕδωρ, water, and γεν.

may be cut by scratching with a file, and then applying a little force with both hands. It may be softened and bent, when of small dimensions, by the flame of a spirit-lamp, or a candle, or, better, by a gas jet. Corks may be perforated by a heated wire, and the hole rendered smooth and cylindrical by a round file; or the ingenious cork-borer of Dr. Mohr, now to be had of all instrument-makers, may be used instead. Lastly, in the event of bad fitting, or unsoundness in the cork itself, a little yellow wax melted over the surface, or even a little grease applied with the finger, renders it sound and air-tight, when not exposed to heat.

Hydrogen is colorless, tasteless, and inodorous when quite pure. To obtain it in this condition, it must be prepared from the purest zinc that can be obtained, and passed in succession through solutions of potash and silver nitrate. When prepared from commercial zinc, it has a slight smell, which is due to impurity, and when iron has been used, the odor is very strong and disagreeable. It is inflammable and burns, when kindled, with a pale, yellowish flame, evolving much heat, but very little light. The result of the combustion is water. It is even less soluble in water than oxygen, and has never been liquefied. Although destitute of poisonous properties, it is incapable of sustaining life.

Hydrogen is the lightest substance known; Dumas and Boussingault place its density between 0·0691 and 0·0695,* referred to that of air as unity. The weight of a litre of hydrogen at 0° C., and under a barometric pressure of 0·760 metre, is 0·08961 gram; consequently, a gram of hydrogen occupies a space of 11·15947 litres.† At 15·5° C. (60° F.), and 30 inches barometric pressure, 100 cubic inches weigh 2·14 grains.

Fig. 96.



When a gas is much lighter or much heavier than atmospheric air, it may often be collected and examined without the aid of the pneumatic trough. A bottle or narrow jar may be filled with hydrogen without much admixture of air, by inverting it over the extremity of an upright tube delivering the gas. In a short time, if the supply be copious, the air will be wholly displaced, and the vessel filled. It may now be removed, the vertical position being carefully retained, and closed by a stopper or glass plate. If the mouth of the jar be wide, it must be partially closed by a piece of cardboard during the operation. This method of collecting gases by displacement is often extremely useful. Hydrogen was formerly used for filling air-balloons, being made for the purpose on the spot from zinc or iron and dilute sulphuric acid. Its use is now superseded by that of coal-gas, which may be made very light by employing a high temperature in the manufacture. Although far inferior to pure hydrogen in buoyant power, it is found in practice to possess advantages over that substance, while its greater density is easily compensated by increasing the magnitude of the balloon.

There is a very remarkable property possessed by gases and vapors in general, which is seen in a high degree of intensity in the case of hydrogen; this is what is called *diffusive power*. If two bottles containing gases which do not act chemically upon each other at common temperatures be connected by a narrow tube and left for some time, the gases will be found, at the expiration of a certain period, depending much upon the narrowness of the tube and its length, uniformly mixed, even though they differ greatly in density, and the system has been arranged in a vertical position, with the heavier gas downwards. Oxygen and hydrogen can thus be made to mix, in a few hours, against the action of gravity, through a tube a yard in

* Ann. Chim. Phys., 3d series, viii. 201.

† As a near approximation, it may be remembered that a litre of hydrogen weighs 0·09 gram, or 9 centigrams, and a gram of hydrogen occupies 11·1 litres.

length, and not more than one quarter of an inch in diameter: and the fact is true of all other gases which are destitute of direct action upon each other.

If a vessel be divided into two portions by a diaphragm or partition of porous earthenware or dry plaster of Paris, and each half filled with a different gas, diffusion will immediately commence through the pores of the dividing substance, and will continue until perfect mixture has taken place. All gases, however, do not permeate the same porous body, or, in other words, do not pass through narrow orifices with the same degree of facility. Professor Graham, to whom we are indebted for a very valuable investigation of this interesting subject, has established the existence of a very simple relation between the rapidity of diffusion and the density of the gas, which is expressed by saying that the diffusive power varies inversely as the square root of the density of the gas itself. Thus, in the experiment supposed, if one half of the vessel be filled with hydrogen and the other half with oxygen, the two gases will penetrate the diaphragm at very different rates; four cubic inches of hydrogen will pass into the oxygen side, while one cubic inch of oxygen travels in the opposite direction. The densities of the two gases are to each other in the proportion of 1 to 16; their relative rates of diffusion will be inversely as the square roots of these numbers, *i. e.*, as 4 to 1.

In order, however, that this law may be accurately observed, it is necessary that the porous plate be very thin; with plates of stucco an inch thick or more, which really consist of a congeries of long capillary tubes, a different law of diffusion is observed.* An excellent material for diffusion experiments is the artificially compressed graphite of Mr. Brockedon, of the quality used for making writing-pencils. It may be reduced by cutting and grinding to the thickness of a wafer, but still retains considerable tenacity. The pores of this substance appear to be so small as entirely to prevent the transmission of gases in mass, so that, to use the language of Mr. Graham, it acts like a molecular sieve, allowing only molecules to pass through.

Fig. 97.

The simplest and most striking method of exhibiting the phenomenon of diffusion is by the use of Graham's diffusion-tube. This is merely a piece of wide glass tube ten or twelve inches long, having one of its extremities closed by a plate of plaster of Paris about half an inch thick, and well dried. When the tube is filled by displacement with hydrogen, and then set upright in a glass of water, the level of the liquid rises in the tube so rapidly, that its movement is apparent to the eye, and speedily attains a height of several inches above the water in the glass. The gas is actually rarefied by its superior diffusive power over that of the external air.

It is impossible to over-estimate the importance in the economy of Nature of this very curious law affecting the constitution of gaseous bodies: it is the principal means by which the atmosphere is preserved in a uniform state, and the accumulation of poisonous gases and exhalations in towns and other confined localities prevented.

A partial separation of gases and vapors of unequal diffusibility may be effected by allowing the mixture to permeate through a plate of graphite or porous earthenware into a vacuum. This effect, called *atmolysis*, is best exhibited by means of an instrument called the *tube-atmolyser*. This is simply a narrow tube of unglazed earthenware, such as a tobacco-pipe stem, two feet long, which is placed within a shorter tube of glass, and secured in its

* See Bunsen's Gasometry, p. 203; Graham's Elements of Chemistry, 2d ed., ii. 624; Watts's Dictionary of Chemistry, ii. 815.

position by corks. The glass tube is connected with an air-pump, and the annular space between the two tubes is made as nearly vacuous as possible. Air or other mixed gas is then allowed to flow along the clay tube in a slow stream, and collected as it issues. The gas or air atmolysed is, of course, reduced in volume, much gas penetrating through the pores of the clay tube into the air-pump vacuum, and the lighter gas diffusing the more rapidly, so that the proportion of the denser constituent is increased in the gas collected. In one experiment, the proportion of oxygen in the air, after traversing the atmolyser, was increased from 20·8 per cent., which is the normal proportion, to 24·5 per cent. With a mixture of oxygen and hydrogen, the separation is, of course, still more considerable.*

A distinction must be carefully drawn between real diffusion through small apertures, and the apparently similar passage of gases through membranous diaphragms, such as caoutchouc, bladder, gold-beater's skin, etc. In this mode of passage, which is called *osmose*, the rate of interchange depends partly on the relative diffusibilities of the gases, partly on the different degrees of adhesion exerted by the membrane on the different gases, by virtue of which the gas which adheres most powerfully penetrates the diaphragm most easily and, attaining the opposite surface, mixes with the other. A sheet of caoutchouc tied over the mouth of a wide-mouthed bottle filled with hydrogen, is soon pressed inwards, even to bursting. If the bottle be filled with air, and placed in an atmosphere of hydrogen, the swelling and bursting takes place outwards. If the membrane is moist, the result is likewise affected by the different solubilities of the gases in the water or other liquid which wets it. For example, the diffusive power of carbonic acid into atmospheric air is very small, but it passes into the latter through a wet bladder with the utmost ease,in virtue of its solubility in the water with which the membrane is moistened. It is by such a process that the function of respiration is performed; the aëration of the blood in the lungs, and the disengagement of the carbonic acid, are effected through wet membranes; the blood is never brought into actual contact with the air, but receives its supply of oxygen, and disembarrasses itself of carbonic acid, by this kind of spurious diffusion.

The high diffusive power of hydrogen against air renders it impossible to retain that gas for any length of time in a bladder or caoutchouc bag; it is even unsafe to keep it long in a gas-holder, lest it should become mixed with air by slight accidental leakage, and rendered explosive.

The passage of gases through membranes like caoutchouc or varnished silk, as well as through wet membranes like bladder, appears to depend upon an actual liquefaction of the gases, which then become capable of penetrating the substance of the membrane (as ether and naphtha do), and may again evaporate on the surface and appear as gases. The unequal absorption of gases in this manner often effects a much more complete separation of the components of a gaseous mixture than can be attained by the atmolytic method above described. Thus, Graham has shown that oxygen is absorbed and condensed by caoutchouc two-and-a-half times more abundantly than nitrogen, and that when one side of a caoutchouc film is freely exposed to the air, while a vacuum is produced on the other side, the film allows 41·6 per cent. of oxygen to pass through, instead of 21 per cent. usually present in the air, so that the air which passes through is capable of rekindling wood burning without flame.

Even metals appear to possess this power of absorbing and liquefying gases. Deville and Troost have observed the remarkable fact that hydrogen gas is capable of penetrating platinum and iron tubes at a red heat, and Graham is of opinion that this effect may be connected with a power resident in these and certain other metals to absorb and liquefy hydrogen, possibly in its character as a metallic vapor. Platinum in the form of

* Graham, Phil. Trans. 1863.

wire or plate, at a low red heat, can take up 3·8 volumes of hydrogen measured cold, and palladium foil condenses as much as 643 times its volume of hydrogen at a temperature below 100° C. In the form of sponge, platinum absorbed 1·48 times its volume of hydrogen, and palladium 90 volumes. This absorption of gases by metals is called *occlusion.**

The meteoric iron of Lenarto contains a considerable quantity of occluded hydrogen. When placed in a good vacuum, it yields 2·85 times its volume of gas, of which 85·68 per cent. consist of hydrogen, with 4·46 carbon monoxide and 9·86 nitrogen. Now, hydrogen has been recognized by spectrum analysis in the light of the fixed stars, and constitutes, according to the observations of father Secchi, the principal element in the atmosphere of a numerous class of stars. "The iron of Lenarto," says Mr. Graham, "has, no doubt, come from such an atmosphere, in which hydrogen greatly prevailed. This meteorite may be looked upon as holding imprisoned within it, and bringing to us, the hydrogen of the stars."†

The rates of *effusion* of gases, that is to say, their rates of passage through a minute aperture in a thin plate of metal or other substance into a vacuum, follow the same law as their rates of diffusion, that is to say, they are inversely as the square roots of the densities of the gases. Nevertheless, the phenomena of diffusion and effusion are essentially different in their nature, the effusive movement affecting masses of a gas, whereas the diffusive movement affects only molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times greater than by the latter. Mixed gases are effused at the same rates as one gas of the actual density of the mixture: and no separation of the gases occurs, as in *diffusion* into a vacuum.

The law of effusion just stated is true only under the condition that the gas shall pass through a minute aperture in a very thin plate. If the plate be thicker, so that the aperture becomes a tube, very different rates of efflux are observed; and when the capillary tube becomes considerably elongated, so that its length exceeds its diameter at least 400 times, the rates of flow of different gases into a vacuum again assume a constant ratio to each other, following, however, a law totally distinct from that of effusion. The principal general results observed with relation to this phenomenon of "Capillary Transpiration" are as follows:—

1. The rate of transpiration of the same gas increases, *cæteris paribus*, directly as the pressure: in other words, equal volumes of gas at different densities require times inversely proportional to their densities. 2. With tubes of equal diameter, the volume transpired in equal times is inversely as the length of the tube. 3. As the temperature rises, the transpiration of equal volumes becomes slower. 4. The rates of transpiration of different gases bear a constant relation to each other, totally independent of their densities, or, indeed, of any known property of the gases. Equal *weights* of oxygen, nitrogen, and carbon monoxide are transpired in equal times; so likewise are equal weights of nitrogen, nitrogen dioxide, and carbon monoxide; and of hydrogen chloride, carbon dioxide, and nitrogen monoxide.‡

COMBINATION OF HYDROGEN WITH OXYGEN.

It has been already stated that, although the light emitted by the flame of pure hydrogen is exceedingly feeble, yet the temperature of the flame is very high. The temperature may be still further exalted by previously mixing the hydrogen with as much oxygen as it requires for combination,

* Graham, Phil. Trans. 1866; Journal of the Chemical Society, [2] v. 235.
† Proceedings of the Royal Society, xv. 502
‡ Graham, Phil. Trans. 1846, p. 591; and 1849, p. 349; also Elements of Chemistry, 2d ed. i. 82.

that is, as will presently be seen, with half its volume. Such a mixture burns like gunpowder, independently of the external air. When raised to the temperature required for combination, the two gases unite with explosive violence. If a strong bottle, holding not more than half a pint, be filled with such a mixture, the introduction of a lighted match or red-hot wire determines in a moment the union of the gases. By certain precautions, a mixture of oxygen and hydrogen can be burned at a jet without communication of fire to the contents of the vessel; the flame is in this case *solid.*

A little consideration will show, that all ordinary flames burning in the air or in pure oxygen are, of necessity, hollow. The act of combustion is nothing more than the energetic union of the substance burned with the surrounding oxygen; and this union can take place only at the surface of the burning body. Such is not the case, however, with the flame now under consideration; the combustible and the oxygen are already mixed, and only require to have their temperature a little raised to cause them to combine in every part. The flame so produced is very different in physical characters from that of a simple jet of hydrogen or any other combustible gas; it is long and pointed, and very remarkable in appearance.

The safety-jet of Mr. Hemming, the construction of which involves a principle not yet discussed, may be adapted to a common bladder containing the mixture, and held under the arm, and the gas forced through the jet by a little pressure. Although this jet, properly constructed, is believed to be safe, it is best to use nothing stronger than a bladder, for fear of injury in the event of an explosion. The gases are often contained in separate reservoirs, a pair of large gas-holders, for example, and only suffered to mix in the jet itself, as in the contrivance of Professor Daniell: in this way all danger is avoided. The eye speedily becomes accustomed to the peculiar appearance of the true hydro-oxygen flame, so as to permit the supply of each gas to be exactly regulated by suitable stop-cocks attached to the jet (fig. 98).

Fig. 98.

Fig. 99.

A piece of thick platinum wire introduced into the flame of the hydro-oxygen blowpipe melts with the greatest ease; a watch-spring or small

steel file burns with the utmost brilliancy, throwing off showers of beautiful sparks; an incombustible oxidized body, as magnesia or lime, becomes so intensely ignited as to glow with a light insupportable to the eye, and to be susceptible of employment as a most powerful illuminator, as a substitute for the sun's rays in the solar microscope, and for night-signals in trigonometrical surveys.

If a long glass tube, open at both ends, be held over a jet of hydrogen (fig. 99), a series of musical sounds are sometimes produced by the partial extinction and rekindling of the flame by the ascending current of air. These little explosions succeed each other at regular intervals, and so rapidly as to give rise to a musical note, the pitch depending chiefly upon the length and diameter of the tube.

Although oxygen and hydrogen may be kept mixed at common temperatures for any length of time, without combination taking place, yet, under particular circumstances, they unite quietly and without explosion. Many years ago, Professor Döbereiner, of Jena, made the curious observation, that finely divided platinum possessed the power of determining the union of the gases; and, more recently, Mr. Faraday has shown that the state of minute division is by no means indispensable, since rolled plates of the metal have the same property, provided their surfaces are absolutely clean. Neither is the effect strictly confined to platinum; other metals, as palladium and gold, and even stones and glass, exhibit the same property, although to a far inferior degree, since they often require to be aided by a little heat. When a piece of platinum-foil, which has been cleaned by hot oil of vitriol and thorough washing with distilled water, is thrust into a jar containing a mixture of oxygen and hydrogen standing over water, combination of the two gases immediately begins, and the level of the water rapidly rises, while the platinum becomes so hot that drops of water accidentally falling upon it enter into ebullition. If the metal be very thin and exceedingly clean, and the gases very pure, its temperature rises after a time to actual redness, and the residue of the mixture explodes. But this is an effect altogether accidental, and dependent upon the high temperature of the platinum, which high temperature has been produced by the preceding quiet combination of the two bodies. When the platinum is reduced to a state of minute division, and its surface thereby much extended, it becomes immediately red-hot in a mixture of hydrogen and oxygen, or hydrogen and air; a jet of hydrogen thrown upon a little of the spongy metal, contained in a glass or capsule, is at once kindled, and on this principle machines for the production of instantaneous light have been constructed. These, however, act well only when constantly used; the spongy platinum is apt to become damp by absorption of moisture from the air, and its power is then for the time lost.

The best explanation that can be given of these curious effects is to suppose that solid bodies in general have, to a greater or less extent, the property of condensing gases upon their surfaces, or even liquefying them (as shown p. 139), and that this faculty is exhibited preëminently by certain of the non-oxidizable metals, as platinum and gold. Oxygen and hydrogen may thus, under these circumstances, be brought, as it were, within the sphere of their mutual attractions by a temporary increase of density, whereupon combination ensues.

Coal-gas and ether or alcohol vapor may be made to exhibit the phenomenon of quiet oxidation under the influence of this remarkable surface-action. A close spiral of slender platinum wire, a roll of thin foil, or even a common platinum crucible, heated to dull redness, and then held in a jet of coal-gas, becomes strongly ignited, and remains in that state as long as the supply of mixed gas and air is kept up, the temperature being maintained by the heat disengaged in the act of union. Sometimes the metal becomes white-hot, and then the gas takes fire.

A very pleasing experiment may be made by attaching such a coil of wire to a cord, and suspending it in a glass containing a few drops of ether, having previously made it red-hot in the flame of a spirit-lamp. The wire continues to glow until the oxygen of the air is exhausted, giving rise to the production of an irritating vapor which attacks the eyes. The combustion of the ether is in this case but partial; a portion of its hydrogen is alone removed, and the whole of the carbon left untouched.

Fig. 100.

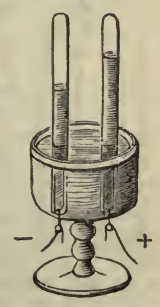
A coil of thin platinum wire may be placed over the wick of a spirit-lamp, or a ball of spongy platinum sustained just above the cotton: on lighting the lamp, and then blowing it out as soon as the metal appears red-hot, slow combustion of the spirit drawn up by the capillarity of the wick will take place, accompanied by the pungent vapors just mentioned, which may be modified, and even rendered agreeable, by dissolving in the liquid some sweet-smelling essential oil or resin.

Hydrogen forms numerous compounds with other bodies, although it is greatly surpassed in this respect, not only by oxygen, but by many of the other elements. The chemical relations of hydrogen tend to place it among the metals. The great discrepancy in physical properties is perhaps more apparent than real. Hydrogen is not yet known in the solid state, while, on the other hand, the vapor of the metal mercury is as transparent and colorless as hydrogen itself. This vapor is only about seven times heavier than atmospheric air, so that the difference in this respect is not nearly so great as that in the other direction between air and hydrogen.

There are two oxides of hydrogen — namely, *water*, and a very peculiar substance, discovered in the year 1818 by M. Thénard, called *hydrogen dioxide*.

It appears that the composition of water was first demonstrated in the year 1781 by Cavendish; * but the discovery of the exact proportions in which oxygen and hydrogen unite in generating that most important compound has, from time to time to the present day, occupied the attention of some of the most distinguished cultivators of chemical science. There are two distinct methods of research in chemistry — the *analytical*, or that in which the compound is resolved into its elements, and the *synthetical*, in which the elements are made to unite and produce the compound. The first method is of much more general application than the second; but in this particular instance both may be employed, although the results of the synthesis are the more valuable.

Fig. 101.



The decomposition of water may be effected by voltaic electricity. When water is acidulated so as to render it a conductor,† and a portion interposed between a pair of platinum plates connected with the extremities of a voltaic apparatus of moderate power, decomposition of the liquid takes place in a very interesting manner; oxygen, in a state of perfect purity, is evolved from the water in contact with the plate belonging to the copper end of the battery, and hydrogen, equally pure, is disengaged at the plate con-

* A claim to the discovery of the composition of water, on behalf of James Watt, has been very strongly urged, and supported by such evidence that the reader of the controversy may be led to the conclusion that the discovery was made by both parties, nearly simultaneously, and unknown to each other. See the article "Gas," by Dr. Paul, in Watts's Dictionary of Chemistry, ii. 780.

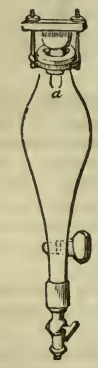
† See the section on "Electro-chemical Decomposition."

nected with the zinc extremity, the middle portions of liquid remaining apparently unaltered. By placing small graduated jars over the platinum plates, the gases can be collected, and their quantities determined. The whole arrangement is shown in fig. 101; the conducting wires pass through the bottom of the glass cup, and away to the battery.

When this experiment has been continued a sufficient time, it will be found that the volume of the hydrogen is a *very* little above twice that of the oxygen: were it not for the accidental circumstance of oxygen being sensibly more soluble in water than hydrogen, the proportion of two to one by measure would come out exactly.

Water, as Mr. Grove has shown, is likewise decomposed into its constituents by heat. The effect is produced by introducing platinum balls, ignited by electricity or other means, into water or steam. The two gases are obtained in very small quantities at a time.

Fig. 102.



When oxygen and hydrogen, both as pure as possible, are mixed in the proportions mentioned, passed into a strong glass tube standing over mercury, and exploded by the electric spark, all the mixture disappears, and the mercury is forced up into the tube, filling it completely. The same experiment may be made with the explosion-vessel or eudiometer of Cavendish (fig. 102). The instrument is exhausted at the air-pump, and then filled from a capped jar with the mixed gases; on passing an electric spark by the wires shown at *a*, explosion ensues, and the glass becomes bedewed with moisture; and if the stop-cock be then opened under water, the latter will rush in and fill the vessel, leaving merely a bubble of air, the result of imperfect exhaustion.

The process upon which most reliance is placed, is that in which pure copper oxide is reduced at a red-heat by hydrogen, and the water so formed is collected and weighed. This oxide suffers no change by heat alone, but the momentary contact of hydrogen, or any common combustible matter, at a high temperature, suffices to reduce a corresponding portion to the metallic state. Fig. 103 will serve to convey some idea of the arrangement adopted in researches of this kind.

A copious supply of hydrogen is procured by the action of dilute sulphuric acid upon the purest zinc that can be obtained; the gas is made to pass in succession through solutions of silver and strong caustic potash, by which its purification is completed. After this it is conducted through a tube three or four inches in length, filled with fragments of pumice-stone steeped in concentrated oil of vitriol, or with anhydrous phosphoric acid. These substances have so great an attraction for aqueous vapor, that they dry the gas completely during its transit. The extremity of this tube is shown at *a*. The dry hydrogen thus arrives at the part of the apparatus containing the copper oxide represented at *b;* this consists of a two-necked flask of very hard white glass, maintained at a red-heat by a spirit-lamp placed beneath. As the decomposition proceeds, the water produced by the reduction of the oxide begins to condense in the second neck of the flask, whence it drops into the receiver *c*, provided for the purpose. A second desiccating tube prevents the loss of aqueous vapor by the current of gas which passes in excess.

Before the experiment can be commenced, the copper oxide, the purity of which is well ascertained, must be heated to redness for some time in a

current of dry air; it is then suffered to cool, and very carefully weighed with the flask. The empty receiver and second drying-tube are also weighed, the disengagement of gas set up, and when the air has been displaced, heat

Fig. 103.

is slowly applied to the oxide. The action is at first very energetic; the oxide often exhibits the appearance of ignition; but as the decomposition proceeds, it becomes more sluggish, and requires the application of a considerable heat to effect its completion.

When the process is at an end, and the apparatus perfectly cool, the stream of gas is discontinued, dry air is drawn through the whole arrangement, and, lastly, the parts are disconnected and reweighed. The loss of the copper oxide gives the oxygen; the gain of the receiver and its drying-tube indicates the water; and the difference between the two, the hydrogen.

A set of experiments, made in Paris in the year 1820,* by Dulong and Berzelius, gave as a mean result, for the composition of water by weight, 8·009 parts oxygen to 1 part hydrogen; numbers so nearly in the proportion of 8 to 1, that the latter have usually been assumed to be true.

More recently the subject has been reinvestigated by Dumas,† with the most scrupulous precision, and the above supposition fully confirmed. The composition of water may therefore be considered as established; it contains by weight 8 parts oxygen to 1 part hydrogen, and by measure, 1 volume oxygen to 2 volumes hydrogen. The densities of the gases, as already mentioned, correspond very closely with these results.

The physical properties of water are too well known to need lengthened description: it is, when pure, colorless and transparent, destitute of taste and odor, and an exceedingly bad conductor of electricity of low tension. It attains its greatest density towards 4·5° C. (40° F.), freezes at 0° C. (32° F.),‡ and boils under the ordinary atmospheric pressure at or near 100° C. (212° F.). It evaporates at all temperatures.

The weight of a cubic centimetre of water at the maximum density is chosen as the unit of weight of the metrical system, and called a *gram;* consequently a litre or cubic decimetre = 100 cubic centimetres of water, at the same temperature, weighs 1000 grams, or 1 kilogram.

A cubic inch of water at 16·7° C. (62° F.) weighs 252·45 grains; a cubic foot weighs nearly 1000 ounces avoirdupois; and an imperial gallon weighs 70,000 grains, or 10 lbs. avoirdupois. Water is 825 times heavier than air. To all ordinary observations, it is incompressible; very accurate experiments have nevertheless shown that it does yield to a small extent when the power employed is very great, the diminution of volume for each atmosphere of pressure being about 51-millionth of the whole.

Clear water, although colorless in small bulk, is blue like the atmosphere when viewed in mass. This is seen in the deep ultramarine tint of the

* Ann. Chim. Phys. xv. 386. † Ibid. 3d series, viii. 189.

‡ According to Dufour, the specific gravity of ice is 0 9175; water, therefore, on freezing, expands by $\frac{1}{11}$th of its volume.

ocean, and perhaps in a still more beautiful manner in the lakes of Switzerland and other Alpine countries, and in the rivers which issue from them, the slightest admixture of mud or suspended impurity destroying the effect. The same magnificent color is visible in the fissures and caverns found in the ice of the glaciers, which is usually extremely pure and transparent within, although foul upon the surface.

The specific gravity of steam or vapor of water is found by experiment to be 0·625, compared with air at the same temperature and pressure, or 9 as compared with hydrogen. Now, it has been already shown that water is composed of two volumes of hydrogen and one volume of oxygen; and if the weight of one volume of hydrogen be taken as unity, that of two volumes hydrogen (= 2) and one volume oxygen (= 16) will together make 18, which is the weight of two volumes of water-vapor. Consequently *water in the state of vapor consists of two volumes of hydrogen and one volume of oxygen condensed into two volumes.* A method of demonstrating this important fact by direct experiment has been devised by Dr. Hofmann. It consists in exploding a mixture of two volumes hydrogen and one volume oxygen, by the electric spark, in a eudiometer tube enclosed in an atmosphere of the vapor of a liquid (amylic alcohol) which boils at a temperature considerably above that of boiling water, so that the water produced by the combination of the gases remains in the state of vapor instead of at once condensing to the liquid form. It is then seen that the three volumes of mixed gas are reduced after the explosion to two volumes.*

Water seldom or never occurs in nature in a state of perfect purity: even the rain which falls in the open country contains a trace of ammoniacal salt, while rivers and springs are invariably contaminated to a greater or less extent with soluble matters, saline and organic. Simple filtration through a porous stone or a bed of sand will separate suspended impurities, but distillation alone will free the liquid from those which are dissolved. In the preparation of distilled water, which is an article of large consumption in the scientific laboratory, it is proper to reject the first portions which pass over, and to avoid carrying the distillation to dryness. The process may be conducted in a metal still furnished with a worm or condenser of silver or tin; lead must not be used.

The ocean is the great recipient of the saline matter carried down by the rivers which drain the land: hence the vast accumulation of salts. The following table will serve to convey an idea of the ordinary composition of sea-water; the analysis is by Dr. Schweitzer,† of Brighton, the water being that of the British Channel:

1000 grains contained—	
Water	964·745
Sodium Chloride	27·059
Potassium Chloride	0·766
Magnesium Chloride	3·666
Magnesium Bromide	0·029
Magnesium Sulphate	2·296
Calcium Sulphate	1·406
Calcium Carbonate	0·033
Traces of Iodine and Ammoniacal salt	··
	1000·000

Its specific gravity was found to be 1·0274 at 15·5 C. (60° F.).
Sea-water is liable to variations of density and composition by the influ-

* For a description of the apparatus, see Hofmann's "Modern Chemistry" (1865), p. 51.
† Philosophical Magazine, July, 1839.

ence of local causes, such as the proximity of large rivers, or masses of melting ice, and other circumstances.

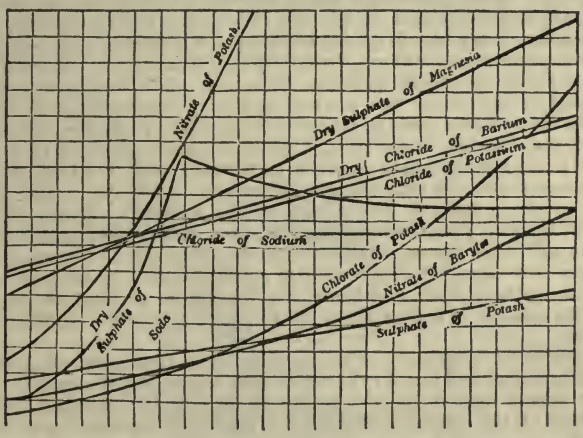
Natural springs are often impregnated to a great extent with soluble substances derived from the rocks they traverse: such are the various mineral waters scattered over the whole earth, and to which medicinal virtues are attributed. Some of these hold ferrous oxide in solution, and are effervescent from carbonic acid gas; others are alkaline, probably from traversing rocks of volcanic origin; some contain a very notable quantity of iodine or bromine. Their temperatures, also, are as variable as their chemical nature. A tabular notice of some of the most remarkable of these waters will be found in the Appendix.

Water enters into direct combination with other bodies, forming a class of compounds called *hydrates;* the action is often very energetic, much heat being evolved, as in the case of the slaking of lime, which is really the production of a hydrate of that base. Sometimes the attraction between the water and the second body is so great that the compound is not decomposable by any heat that can be applied; the hydrates of potash and soda, and of phosphoric oxide, furnish examples. Oil of vitriol is a hydrate of sulphuric oxide, from which the water cannot be thus separated.

Water very frequently combines with saline substances in a less intimate manner than that above described, constituting what is called *water of crystallization*, from its connection with the geometrical figure of the salt. In this case it is easily driven off by the application of heat.

Lastly, the solvent properties of water far exceed those of any other liquid known. Among salts a very large proportion are soluble to a greater or less extent, the solubility usually increasing with the temperature, so that a hot saturated solution deposits crystals on cooling. There are a few exceptions to this law, one of the most remarkable of which is com-

Fig. 104. — *Solubility of Salts in* 100 *parts of Water.*



mon salt, the solubility of which is nearly the same at all temperatures: the hydrate and certain organic salts of calcium, also, dissolve more freely in cold than in hot water.

The diagram (fig. 104) exhibits the unequal solubility of different salts in water of different temperatures. The *lines of solubility* cut the verticals raised from points indicating the temperatures, upon the lower horizontal line, at heights proportioned to the quantities of salt dissolved by 100 parts of water. The diagram shows, for example, that 100 parts of water dissolve, of potassium sulphate 3 pts. at 0° C., 17 pts. at 50°, and 26 pts. at 100°. There are salts which, like sodium chloride, possess, as already mentioned, very nearly the same degree of solubility in water at all temperatures; in others, like potassium sulphate or potassium chloride, the solubility increases directly with the increment of temperature; in others, again, like potassium nitrate or potassium chlorate, the solubility augments much more rapidly than the temperature. The diagram exhibits the differences in the deportment of these different salts very conspicuously, by a straight horizontal line, by a straight inclined line, and lastly by curves, the convexity of which is turned toward the lower horizontal line.

In the diagram, the solubility of salt is represented by the quantity of anhydrous salt dissolved by 100 parts of water. This is, in fact, the common mode of stating the solubility of salts. It is obvious, however, that salts containing water of hydration or water of crystallization cannot, within certain limits of temperature, dissolve in water in the anhydrous state, but must be dissolved as hydrates. The solubility of a hydrated salt frequently differs very considerably from that of the same salt in the anhydrous state. Again, many salts form more than one hydrate; and these several hydrates may also differ in their solubility. Sodium sulphate forms a peculiar hydrate, consisting, in 100 parts, of 53 parts of anhydrous salt and 47 parts of water, which is obtained in crystals, when a solution of sodium sulphate, saturated at 100° C. (212° F.), is considerably cooled out of contact with the air: this hydrate is much more soluble than Glauber's salt, the other hydrate of sodium sulphate, which differs from the former one in its crystalline form, and consists, in 100 parts, of 44·2 parts of anhydrous salt and 55·8 parts of water. When a solution of sodium sulphate is saturated at the boiling-point of water, and cooled to the common temperature without depositing any crystals, the salt exists in the form of the more soluble hydrate. This salt, when coming in contact with the dust of the air, or with a small crystal of common Glauber's salt, is suddenly transformed into the less soluble hydrate, part of which separates from the solution, in the form of Glauber's salt. From 0° to 33° C. (32° to 91° F.) sodium sulphate dissolves as Glauber's salt, the solubility of which increases with the temperature; hence the rapid rise of the curve representing the solubility of the salt in the diagram. Above 33° C. (91° F.) the hydrate of sodium sulphate is, even in solution, decomposed, being more and more thoroughly converted into the anhydrous salt as the temperature increases. Sodium sulphate appears, however, far less soluble in the anhydrous state, and hence the diminution of solubility of the salt when its solution is heated above 33° C. (91° F.), which is exhibited by the diagram.

Liquid Diffusion. Dialysis. — When a solution having a sp. gr. greater than water is introduced into a cylindrical glass vessel, and then water very cautiously poured upon it, in such a manner that the two layers of liquid remain unmoved, the substance dissolved in the lower liquid will gradually pass into the supernatant water, though the vessel may have been left undisturbed, and the temperature remain unchanged. This gradual passage of a dissolved substance from its original solution into pure water, taking place notwithstanding the higher specific gravity of the substance which opposes this passage, is called the *diffusion of liquids*. The phenomena of this diffusion have been lately investigated by Mr. Graham, who has arrived at very important results. Different substances, when in solution of the same

concentration, and under other similar circumstances, diffuse with very unequal velocity. Hydrochloric acid, for instance, diffuses with greater rapidity than potassium chloride, potassium chloride more rapidly than sodium chloride, and the latter, again, more quickly than magnesium sulphate; gelatin, albumin, and caramel diffuse very slowly. Diffusion is generally found to take place more rapidly at high than at low temperatures. Diffusion is more particularly rapid with crystallized substances, though not exclusively, for hydrochloric acid and alcohol are among the highly diffusive bodies. Diffusion is slow with non-crystalline bodies, which, like gelatin, are capable of forming a jelly, though even here exceptions are met with. Mr. Graham calls the substances of great diffusibility *crystalloïds*, the substances of low diffusibility *colloïds*. The unequal power of diffusion with which different substances are endowed frequently furnishes the means of separating them. When water is poured with caution, so as to prevent mixing, upon a solution containing equal quantities of potassium chloride and sodium chloride, the more diffusible potassium chloride travels more rapidly upwards than the less diffusible sodium chloride, and very considerable portions of potassium chloride will have reached the upper layers of the water before the sodium chloride has arrived there in appreciable quantity. The separation of rapidly diffusible crystalloïds and slowly diffusible colloïds succeeds still better.

A more perfect separation of crystalloïds and colloïds may be accomplished in the following manner: Mr. Graham has made the important observation, that certain membranes, and also parchment paper, when in contact, on the one surface, with a solution containing a mixture of crystalloïdal and colloïdal substances, and, on the other surface, with pure water, will permit the passage to the water of the crystalloïds. but not of the colloïds. To carry out this important mode of separation, which is designated by the term *dialysis*, the lower mouth of a glass vessel, open on both sides (fig. 105), is tied over with parchment paper placed upon an appropriate support (fig. 106), and transferred, together with the latter, into a larger vessel filled with water (fig. 107); or the vessel may be suspended, as shown in fig. 108. The liquid containing the different substances in

Fig. 105.

Fig. 106.

Fig. 107.

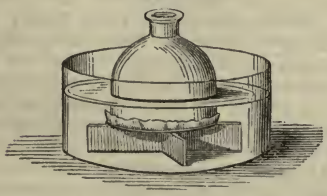
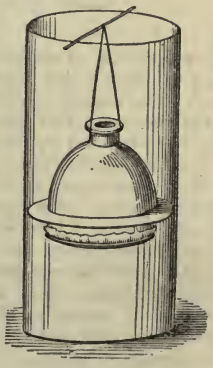


Fig. 108.

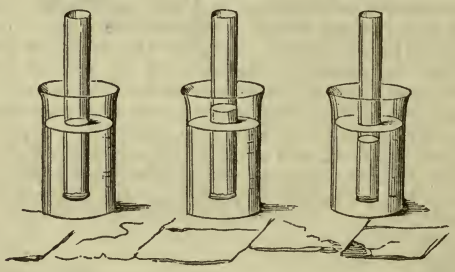


solution is then poured into the inner vessel, so as to form a layer of about half an inch in height upon the parchment paper. The crystalloïdal substances gradually pass through the parchment paper into the outer

water, which may be renewed from time to time: the colloïdal substances are almost entirely retained by the liquid in the inner vessel. In this manner Mr. Graham has prepared several colloïds, free from crystalloïds; he has shown, moreover, that poisonous crystalloïds, such as arsenious acid or strychnine, even when mixed with very large proportions of colloïdal substances, pass over into the water of the dialyzer in such a state of purity that their presence may be established by re-agents with the utmost facility.

Osmose. — When two different liquids are separated by a porous diaphragm, as, for instance, by a membrane, and the liquids mix through this diaphragm, it is found that in most cases the quantities travelling in opposite direction are unequal. Suppose three cylinders, the lower mouths of which are tied over with bladders, filled respectively with concentrated solutions of copper sulphate, sodium chloride, and alcohol, and let them be immersed in vessels containing water to such a depth that the liquids inside and outside are level (fig. 109). After some time the liquid within the tube is found to have risen appreciably above the level of the water (fig. 110). On the other hand, if the cylinder filled with pure water be immersed in a solution of copper sulphate, or of sodium chloride, or in alcohol, the liquid in the cylinder is seen to diminish after some time (fig 111). A larger quantity of water passes through the bladder into the solution of

Fig. 109. *Fig.* 110. *Fig.* 111.



copper sulphate, of sodium chloride, or into alcohol, than the amount of either of these three liquids which passes through the bladder into the water. The mixing of dissimilar substances through a porous diaphragm is called *osmose.* The passage in larger proportion of one liquid into another is designated by the term *exosmose.*

These phenomena are due to the attraction which the two liquids have for each other, and to the difference of the attraction exercised by the diaphragm upon these liquids. Bladder takes up a much larger quantity of water than of a solution of salt or of alcohol. Very rarely only one of the liquids traverses the diaphragm; generally two currents of unequal strength move in opposite directions. When water is separated by an animal membrane from a solution of salt or from alcohol, not only is a transition of water to these liquids observed, but a small quantity of hydrochloric acid and of alcohol also passes over into the water. In some cases, however, when colloïdal substances in concentrated solutions are on one side of the diaphragm and water on the other, the latter alone traverses the diaphragm, not a trace of the former passing through to the water.

Water likewise dissolves gases. Solution of gases in water (or in other liquids) is called *absorption,* unless this solution gives rise to the formation of chemical compounds in definite proportions. The phenomena of absorp-

tion have been more particularly studied by Bunsen, and it is to this philosopher that we are indebted for the most accurate examination of this subject.

Water dissolves very unequal quantities of the different gases and very unequal quantities of the same gas at different temperatures. 1 vol. of water absorbs, at the temperatures stated in the table, and under the pressure of 30 inches of mercury, the following volumes of different gases, measured at 0° C. and 30 inches pressure:

	Oxygen.	Nitrogen.	Hydrogen.	Nitrogen Monoxide.	Carbon Dioxide.
1° C. . .	0·041	0·020	0.019	1·31	1.80
10° . .	0·033	0·016	0·019	0·92	1·18
20° . .	0·028	0·014	0·019	0·67	0·90

	Chlorine.	Hydrogen Sulphide.	Sulphurous Oxide.	Hydrochloric Acid.	Ammonia.
0° C. . .	—	4·37	53·9	505	1180
10° . .	2·59	3·59	36·4	472	898
20° . .	2·16	2·91	27·3	441	680
30° . .	1·75	2·33	20·4	412	536
40° . .	1·37	1·86	15·6	387	444

When the pressure increases, a larger quantity of the gases is absorbed. Gases moderately soluble in water follow in their solubility the law of Henry and Dalton, according to which the quantity of gas dissolved is proportional to the pressure. At 10° C. 1 vol. of water absorbs under a pressure of 1 atmosphere 1·18 vol. of carbon dioxide, measured at 0° and under a pressure of 30 inches mercury. The quantity of carbon dioxide dissolved under a pressure of 2 atmospheres, and measured under conditions precisely similar to those of the previous experiments, equals 2·36 vol. Again, 1 vol. of water dissolves under a pressure of $\frac{1}{2}$ atmosphere, 0.59 vol. of carbon dioxide also measured at 0° and under 30 inches of mercury. Gases which are exceedingly soluble in water do not obey this law, except at higher temperatures, when the solubility has been already considerably diminished.

It deserves, however, to be noticed, that the pressure which determines the rate of absorption of a gas is by no means the general pressure to which the absorbing liquid is exposed, but that pressure which the gas under consideration would exert if it were alone present in the space with which the absorbing liquid is in contact. Thus, supposing water to be in contact with a mixture of 1 vol. of carbon dioxide and 3 vol. of nitrogen, under a pressure of 4 atmospheres, the amount of carbon dioxide dissolved by the water will be by no means equal to that which the water would have absorbed if it had been at the same pressure of 4 atmospheres in contact with pure carbon dioxide. In a mixture of carbon dioxide and nitrogen in the stated proportions, the carbon dioxide exercises only $\frac{1}{4}$, the nitrogen only $\frac{3}{4}$, of the total pressure of the gaseous mixture (4 atmospheres); the partial pressure due to the carbon dioxide is in this case 1 atmosphere, that due to the nitrogen 3 atmospheres; and water, though exposed to a pressure of 4 atmospheres, cannot, under these circumstances, absorb more carbon dioxide than it would if it were in contact with pure carbon dioxide under a pressure of 1 atmosphere.

It is necessary to bear this in mind in order to understand why the air which is absorbed by water out of the atmosphere differs in composition from atmospheric air. The latter consists very nearly of 21 vol. of oxygen and 79 vol. of nitrogen In atmospheric air which acts under a pressure of 1 atmosphere, the oxygen exerts a partial pressure of $\frac{21}{100}$, the nitrogen a

partial pressure of $\frac{79}{100}$ atmosphere. At 10° C. (50° F.) 1 vol. of water (see the above table) absorbs 0·033 vol. of oxygen, and 0·016 vol. of nitrogen, supposing these gases to act in the pure state under a pressure of 1 atmosphere. But under the partial pressures just indicated, water of 10° C. cannot absorb more than $\frac{21}{100} \times 0{\cdot}033 = 0{\cdot}007$ of oxygen, and $\frac{79}{100} \times 0\ 016 = 0{\cdot}013$ vol. of nitrogen. In $0{\cdot}007 + 0{\cdot}013 = 0{\cdot}020$ vol. of gaseous mixture absorbed by water there are consequently 0·007 vol. of oxygen, and 0·013 vol. of nitrogen, or in 20 vol. of this mixture, 7 vol. of oxygen and 13 vol. of nitrogen, or in 100 vol. of the gaseous mixture, 35 vol. of oxygen and 69 vol. of nitrogen. The air contained at the common temperature in water is thus seen to be very much richer in oxygen than ordinary atmospheric air.

Water containing a gas in solution, when exposed in a vacuum or in a space filled with another gas, allows the gas absorbed to escape until the quantity retained corresponds with the share of the pressure belonging to the gas evolved. If the latter be constantly removed by a powerful absorbent or by a good air-pump, it is in most cases easy to separate every trace of gas from the water. The same result is obtained when water containing a gas in solution is exposed in a space of comparatively infinite size filled with another gas. Water in which nitrogen monoxide is dissolved loses the latter entirely by mere exposure to the atmosphere, and the gas evolved cannot, at any moment, exert more than an infinitely small share of the pressure. If water be freed from gases by ebullition, the separation depends partly upon the diminution of the solubility by the increase of temperature, partly also upon the formation above the surface of the liquid of a constantly renewed atmosphere into which the gas still retained by the liquid may escape.

Some gases which are absorbed in large quantities, and very quickly by water, — hydrochloric acid, for instance, — cannot be perfectly expelled either by the protracted action of another gas (exposure to the atmosphere) or by ebullition; in such cases the liquid still charged with gas evaporates as a whole when it has assumed a certain composition. This composition varies, however, if the liquid be submitted to a current of air, with the temperature; and if it be boiled, with the pressure under which ebullition takes place.

Liquids also lose the gas they contain in solution by freezing: hence the air-bubbles in ice, which consist of the air which had been absorbed from the atmosphere by the water. Gas is retained by liquids at the freezing temperature only when it forms a chemical combination in definite proportion with the liquid. Water containing chlorine or sulphurous acid in solution freezes without evolution of gas, with formation of solid hydrates of chlorine or sulphurous acid.

Pure water generally dissolves gases more copiously than water containing solid bodies in solution (salt water, for instance). If in some few cases exceptions are observed to take place, they appear to depend upon the formation of feeble but true chemical compounds in definite proportion; the fact that carbon dioxide is more copiously absorbed by water containing sodium phosphate in solution than by pure water may perhaps be explained in this manner.

When water is heated in a strong vessel to a temperature above that of the ordinary boiling-point, its solvent powers are still further increased. Dr. Turner inclosed in the upper part of a high-pressure steam-boiler, worked at 149° C. (300° F.), pieces of plate and crown glass. At the expiration of four months the glass was found completely corroded by the action of the water; what remained was a white mass of silica, destitute of alkali, while stalactites of siliceous matter, above an inch in length, depended from the little wire cage which enclosed the glass. This experi-

ment tends to illustrate the changes which may be produced by the action of water at a high temperature in the interior of the earth upon felspathic and other rocks. The phenomenon is manifest in the Geyser springs of Iceland, which deposit siliceous sinter.*

Hydrogen Dioxide,† sometimes called *oxygenated water*, is an exceedingly interesting substance, but very difficult of preparation. It is formed by dissolving barium dioxide in dilute hydrochloric acid carefully cooled by ice, and then precipitating the barium by sulphuric acid; the excess of oxygen of the dioxide, instead of being disengaged as gas, unites with a portion of the water, and converts it into hydrogen dioxide. This treatment is repeated with the same solution and fresh portions of the barium dioxide, until a considerable quantity of the latter has been consumed, and a corresponding amount of hydrogen dioxide formed. The liquid yet contains hydrochloric acid, to get rid of which it is treated in succession with silver sulphate and baryta-water. The whole process requires the utmost care and attention. The barium dioxide itself is prepared by exposing pure baryta, contained in a red-hot porcelain tube, to a stream of oxygen. The solution of hydrogen dioxide may be concentrated under the air-pump receiver until it acquires the specific gravity of 1·45. In this state it presents the aspect of a colorless, transparent, inodorous liquid, possessing remarkable bleaching powers. It is very prone to decomposition; the least elevation of temperature causes effervescence, due to the escape of oxygen gas; near 100° it is decomposed with explosive violence. Hydrogen dioxide contains exactly twice as much oxygen as water, or 16 parts to 1 part of hydrogen.

A trioxide of hydrogen is said to exist, although it has never been obtained in the pure state. It is likewise a powerful oxidizing agent, and altogether similar in its properties to the dioxide. According to the researches of Dr. Baumert, minute quantities of this substance are formed in the decomposition of water by electricity, and impart the odor by which the products of this process are characterized; but, according to the experiments of Andrews and others, already referred to (p. 135), the supposed trioxide really consists of active oxygen or ozone, with a small quantity of hydrogen dioxide.

NITROGEN.

Nitrogen ‡ constitutes about four-fifths of the atmosphere, and enters into a great variety of combinations. It may be prepared by several methods. One of the simplest of these is to burn out the oxygen from a confined portion of air by phosphorus, or by a jet of hydrogen.

A small porcelain capsule is floated on the water of the pneumatic trough, and a piece of phosphorus is placed in it and set on fire. A bell-jar is then inverted over the whole, and suffered to rest on the shelf of the

* Philosophical Magazine, Oct. 1834.

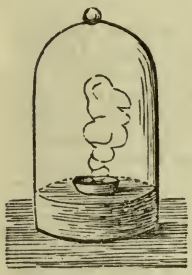
† In symbols the composition of water and hydrogen dioxide is thus expressed:—

Water . . . . . OH_2.
Hydrogen dioxide . . . . . O_2H_2.

‡ *I. e.* Generator of nitre; also called Azote, from *a*, privative, and $\zeta\omega\acute{\eta}$, life.

trough, so as to project a little over its edge. At first the heat causes expansion of the air of the jar, and a few bubbles are expelled, after which the level of the water rises considerably. When the phosphorus becomes extinguished by exhaustion of the oxygen, and time has been given for the subsidence of the cloud of finely divided snow-like phosphoric oxide which floats in the residual gas, the nitrogen may be transferred into another vessel, and its properties examined.

Fig. 112.



Prepared by the foregoing process, nitrogen is contaminated with a little vapor of phosphorus, which communicates its peculiar odor. A preferable method is to fill a porcelain tube with turnings of copper, or, still better, with the spongy metal obtained by reducing the oxide with hydrogen; to heat this tube to redness, and then pass through it a slow stream of atmospheric air, the oxygen of which is entirely removed during its progress by the heated copper.

If chlorine gas be passed into solution of ammonia, the latter substance, which is a compound of nitrogen with hydrogen, is decomposed; the chlorine combines with the hydrogen, and the nitrogen is set free with effervescence. In this manner very pure nitrogen can be obtained. In making this experiment, it is necessary to stop short of saturating or decomposing the whole of the ammonia; otherwise there will be great risk of accident from the formation of an exceedingly dangerous explosive compound, produced by the contact of chlorine with an ammoniacal salt.

Another very easy and perfectly safe method of obtaining pure nitrogen is to decompose a solution of potassium nitrite with ammonium chloride (sal-ammoniac). The potassium nitrite is prepared by passing the red vapors of nitrous acid obtained by heating dilute nitric acid with starch into a solution of caustic potash. On boiling the resulting solution with sal-ammoniac, nitrogen gas is evolved, while potassium chloride remains in solution.*

Nitrogen is destitute of color, taste, and odor; it is a little lighter than air, its density being, according to Dumas, 0·972. A litre of the gas at 0° C. and 760 mm. barometric pressure weighs 1·25658 gram. 100 cubic inches, at 60° F. and 30 inches barometer, weigh 30·14 grains. Nitrogen is incapable of sustaining combustion or animal existence, although, like hydrogen, it has no positive poisonous properties; neither is it soluble to any notable extent in water or in caustic alkali; it is, in fact, best characterized by negative properties.

The exact composition of the atmosphere has repeatedly been made the subject of experimental research. Besides nitrogen and oxygen, the air contains a little carbon dioxide (carbonic acid), a very variable proportion of aqueous vapor, a trace of ammonia, and, *perhaps*, a little carburetted hydrogen. The oxygen and nitrogen are in a state of mixture, not of combination, yet their ratio is always uniform. Air has been brought from lofty Alpine heights, and compared with that from the plains of Egypt; it has been brought from an elevation of 21,000 feet by the aid of the balloon; it has been collected and examined in London and Paris, and many other places; still the proportion of oxygen and nitrogen remains unaltered, the diffusive energy of the gases being adequate to maintain this perfect uniformity of mixture. The carbon dioxide, on the contrary, being much

* The reaction is represented by the equation,

$$\underset{\text{Potassium nitrite.}}{NO^2K} + \underset{\text{Ammonium chloride.}}{NH^4Cl} = \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Water.}}{2OH_2} + \underset{\text{Nitrogen gas.}}{N_2}$$

influenced by local causes, varies considerably. In the following table the proportions of oxygen and nitrogen are given on the authority of Dumas, and the carbon dioxide on that of De Saussure: the ammonia, the discovery of which in atmospheric air is due to Liebig, is too small in quantity for direct estimation.

Composition of the Atmosphere.

	By weight.	By measure.
Nitrogen	77 parts	79·19
Oxygen	23 "	20·81
	100	100·00

Carbon dioxide, from 3·7 measures to 6·2 measures in 10,000 measures of air.

Aqueous vapor variable, depending much upon the temperature.

Ammonia, a trace.

Dr. Frankland has analyzed samples of air taken by himself in the valley of Chamouni, on the summit of Mont Blanc, and at the Grands Mulets. The following are the results of his analyses:

	Carbon dioxide.	Oxygen.
Chamouni (3000 feet)	0·063	20·894
Grands Mulets (11,000 feet)	0·111	20·802
Mont Blanc (15,732 feet)	0·061	20·963

A litre of pure and dry air at 0° C. and 760 mm. pressure weighs 1·29366 grams. 100 cubic inches at 60° F. and 30 inches barom. weigh 30·935 grains: hence a cubic foot weighs 536·96 grains, which is $\frac{1}{816}$ of the weight of a cubic foot of water at the same temperature.

The analysis of air is very well effected by passing it over finely divided copper contained in a tube of hard glass, carefully weighed and then heated to redness: the nitrogen is suffered to flow into an exhausted glass globe, also previously weighed. The increase of weight after the experiment gives the information sought.

Fig. 113.

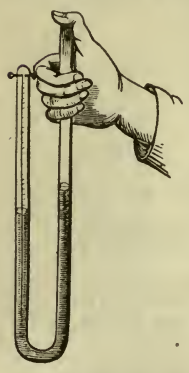
An easier, but less accurate method consists in introducing into a graduated tube, standing over water, a known quantity of the air to be examined, and then passing into the latter a stick of phosphorus affixed to the end of a wire. The whole is left about twenty-four hours, during which the oxygen is slowly but completely absorbed, after which the phosphorus is withdrawn, and the residual gas read off.

Liebig has proposed to use an alkaline solution of pyrogallic acid (a substance which will be described in the department of organic chemistry) for the absorption of oxygen. The absorptive power of such a solution, which turns deep black on coming in contact with the oxygen, is very considerable. Liebig's method combines great accuracy with unusual rapidity and facility of execution.

Another plan is to mix the air with hydrogen and pass an electric spark through the mixture: after explosion the volume of gas is read off and compared with that of the air employed. Since the analysis of gaseous bodies by explosion is an operation of great importance in practical chemistry, it may be worth while describing the process in detail, as it is applicable, with certain obvious variations, to a number of analogous cases.

A convenient form of apparatus for the purpose, when great accuracy is not required, is the syphon eudiometer of Dr. Ure: this consists of a stout glass tube, having an internal diameter of about one third of an inch, closed at one end, and bent into the form represented in fig. 114. Two pieces of platinum wire, melted into the glass near the closed extremity, serve to give passage to the spark. The closed limb is carefully graduated. When required for use, the instrument is filled with mercury, and inverted in a vessel of the same liquid. A quantity of the air to be examined is then introduced, the manipulation being precisely the same as with experiments over water; the open end is stopped with the thumb, and the air transferred to the closed extremity. The instrument is next held upright, and after the level of the mercury has been made equal on both sides by displacing a portion from the open limb by thrusting down a piece of stick, the volume of air is read off. This done, the open part of the tube is again filled up with mercury, closed with the finger, inverted into the liquid metal, and a quantity of pure hydrogen introduced, equal, as nearly as can be guessed, to about half the volume of the air. The eudiometer is once more brought into the erect position, the level of the mercury equalized, and the volume again read off; the quantity of hydrogen added is thus accurately ascertained. All is now ready for the explosion; the instrument is held in the way represented, the open end being firmly closed by the thumb, while the knuckle of the fore-finger touches the nearer platinum wire; the spark is then passed by the aid of a charged jar or a good electrophorus, and the explosion ensues. The air confined by the thumb in the open part of the tube acts as a spring and moderates the explosive effect. Nothing now remains but to equalize the level of the mercury by pouring a little more into the instrument, and then to read off the volume for the last time.

Fig. 114.



What is required to be known from this experiment is the *diminution* the mixture suffers by explosion; for since the hydrogen is in excess, and since that body unites with oxygen in the proportion by measure of two to one, one-third part of that diminution must be due to the oxygen contained in the air introduced. As the amount of the latter is known, the proportion of oxygen it contains thus admits of determination. The case supposed will render this clear.

Air introduced	100 measures.
Air and hydrogen	150
Volume after explosion	87
Diminution	63

$\frac{63}{3} = 21$; oxygen in the hundred measures.

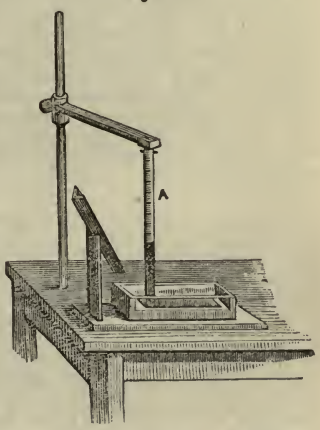
The syphon eudiometer in the simple form above described is not well adapted for accurate analysis, especially when, as in the analysis of many gaseous mixtures, caustic potash and other re-agents have to be introduced into the closed limb, to absorb some of the components of the mixture, or of the products resulting from the explosion; but it forms the essential part of the more exact and complex forms of eudiometer devised by Rég-

nault, and by Frankland and Ward, in which provision is made for accurately adjusting the level of the mercury, and for quickly transferring the gas to another tube in which it may be subjected to the action of absorbing agents, and then returning it to the syphon tube for measurement.*

The simplest, and, on the whole, the most convenient form of eudiometer consists of a straight graduated glass tube (fig. 115) closed at the top, and having platinum wires inserted near the closed end. This tube is filled with mercury, and inverted in a mercurial pneumatic trough.

A quantity of air, sufficient to fill about one sixth of the tube, is then introduced, and its volume accurately ascertained by reading off with a teloscope the number of divisions on the tube to which the mercury reaches, whilst the height of the column of mercury in the tube above the trough, together with that of the barometer, and the temperature of the air, are also read off. A quantity of pure hydrogen gas is now added, more than sufficient to unite with all the oxygen present; and the volume of the gas and the pressure exerted upon it, are then determined as before. An electric spark is now passed through the mixture, care being taken to prevent any escape, by pressing the open end of the eudiometer against a piece of sheet caoutchouc under the mercury in the trough. After the explosion, the volume is again determined as before, and is found to be less than that before the explosion.

Fig. 115.



One third of the diminution gives, as already explained, the volume of oxygen contained in the air taken for analysis.

Compounds of Nitrogen and Oxygen.

There are five distinct compounds of nitrogen and oxygen, thus named and constituted: —

	Composition.			
	By weight.		By volume.	
	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
Nitrogen monoxide†	28	16	2	1
Nitrogen dioxide	28	32	2	2
Nitrogen trioxide, or Nitrous oxide	28	48	2	3
Nitrogen tetroxide	28	64	2	4
Nitrogen pentoxide, or Nitric oxide	28	80	2	5

A comparison of these numbers will show that the quantities of oxygen which unite with a given quantity of nitrogen are to one another in the ratio of the numbers 1, 2, 3, 4, 5.

* See the article "Analysis of Gases," by Dr. Russell, in Watts's "Dictionary of Chemistry," i. 276.

† In symbols the composition of these bodies is thus expressed: —

Nitrogen monoxide . . . N_2O
Nitrogen dioxide . . . . N_2O_2 or NO
Nitrogen trioxide . . . . N_2O_3
Nitrogen tetroxide . . . . N_2O_4 or NO_2
Nitrogen pentoxide . . . N_2O_5.

The third and fifth of the compounds in the table are capable of taking up the elements of water and of metallic oxides to form salts (p. 133), called respectively *nitrites* and *nitrates*, the hydrogen salts being also called *nitrous* and *nitric acid*.* The other three nitrogen oxides do not form salts. It will be convenient to commence the description of these compounds with the last on the list, viz., the pentoxide, as its salts, the nitrates, are the sources from which all the other compounds in the series are obtained.

Nitrogen Pentoxide or Nitric Oxide (also called *Anhydrous Nitric Acid* or *Nitric Anhydride*). — This compound was discovered in 1849 by Deville, who obtained it by exposing silver nitrate, which may be regarded as a compound of nitrogen pentoxide with silver and oxygen, to the action of chlorine gas. Chlorine and silver then combine, forming silver chloride, which remains in the apparatus, while oxygen and nitrogen pentoxide separate.† The latter is a colorless substance, crystallizing in six-sided prisms, which melt at 30° and boil between 45° and 50°, when they begin to decompose. Nitrogen pentoxide sometimes explodes spontaneously. It dissolves in water with great rise of temperature, forming hydrogen nitrate or nitric acid.

Nitrates — Nitric Acid. — In certain parts of India, and in other hot dry climates where rain is rare, the surface of the soil is occasionally covered by a saline efflorescence, like that sometimes apparent on newly plastered walls: this substance collected, dissolved in hot water, and crystallized from the filtered solution, furnishes the highly important salt known in commerce as nitre or saltpetre, and consisting of potassium nitrate. To obtain nitric acid, equal weights of powdered nitre and strong sulphuric acid are introduced into a glass retort, and heat is applied by means of an Argand gas-lamp or charcoal chauffer, (see fig. 38). A flask, cooled by a wet cloth, is adapted to the retort to serve for a receiver. No luting of any kind must be used.

As the distillation advances, the red fumes which first arise disappear, but towards the end of the process they again become manifest. When this happens, and very little liquid passes over, while the greater part of the saline matter of the retort is in a state of tranquil fusion, the operation may be stopped; and when the retort is quite cold, water may be introduced to dissolve out the saline residue. The reaction consists in an interchange between the potassium of the nitre and half the hydrogen of the sulphuric acid (hydrogen sulphate), whereby there are formed hydrogen nitrate which distils over, and hydrogen and potassium sulphate which remains in the retort.‡

In the manufacture of nitric acid on the large scale, the glass retort is replaced by a cast-iron cylinder, and the receiver by a series of earthen condensing vessels connected by tubes. Sodium nitrate, found native in Peru, is now generally substituted for potassium nitrate.

Nitric acid thus obtained has a specific gravity of from 1·5 to 1·52; it has a golden-yellow color, due to nitrogen trioxide, or tetroxide, which is held in solution, and, when the acid is diluted with water, gives rise by its decomposition to a disengagement of nitric oxide. Nitric acid is ex-

* Hydrogen nitrate, or Nitrous acid . . . . . $N_2O_3.OH_2$ or NOH_2
Potassium nitrate . . . . . $N_2O_3.OK_2$ or NOK_2
Hydrogen nitrate, or Nitric acid . . . . . $N_2O_5.OH_2$ or NO_3H
Potassium nitrite . . . . . $N_2O_5.OK_2$ or NO_3K.

† $NO_3Ag + Cl_2 = 2AgCl + O + N_2O_5$.

‡

NO_3K	+	SO_4H_2	=	NO_3H	+	SO_4HK
Potassium nitrate.		Hydrogen sulphate.		Hydrogen nitrate.		Hydrogen and potassium sulphate.

ceedingly corrosive, staining the skin deep yellow, and causing total disorganization. Poured upon red-hot powdered charcoal, it causes brilliant combustion; and when added to warm oil of turpentine, acts upon that substance so energetically as to set it on fire.

Pure nitric acid, in its most concentrated form, is obtained by mixing the above with about an equal quantity of strong sulphuric acid, redistilling, collecting apart the first portion which comes over, and exposing it in a vessel slightly warmed and sheltered from the light, to a current of dry air made to bubble through it, which completely removes the nitrous acid. In this state the product is as colorless as water: it has the sp. gr. 1·517 at 15·5° (60° F.), boils at 84·5° (184° F.), and consists of 54 parts nitrogen pentoxide and 9 parts water. Although nitric acid in a more dilute form acts very violently upon many metals, and upon organic substances generally, this is not the case with the most concentrated acid: even at a boiling heat, it refuses to attack iron or tin; and its mode of action on lignin, starch, and similar substances is quite peculiar and very much less energetic than that of an acid containing more water.

On boiling nitric acid of different degrees of concentration, at the ordinary atmospheric pressure, a residue is left, boiling at 120·5° and 29 inches barometer, and having the sp. gr. 1·414 at 15·5°. This acid was formerly supposed to be a definite compound of nitric acid with water; but Roscoe has recently proved this assumption to be incorrect, the composition of the acid varying according to the pressure under which the liquid boils.

The nitrates form a very extensive and important group of salts, which are remarkable for being all soluble in water. Hydrogen nitrate is of great use in the laboratory, and also in many branches of industry.

The acid prepared in the way described is apt to contain traces of chlorine from common salt in the nitre, and sometimes of sulphate from accidental splashing of the pasty mass in the retort. To discover these impurities, a portion is diluted with four or five times its bulk of distilled water, and divided between two glasses. Solution of silver nitrate is dropped into the one, and solution of barium nitrate into the other; if no change ensue in either case, the acid is free from the impurities mentioned.

Nitric acid has been formed in small quantity by a very curious process, namely, by passing a series of electric sparks through a portion of air in contact with water or an alkaline solution. The amount of acid so formed after many hours is very minute; still it is not impossible that powerful discharges of atmospheric electricity may sometimes occasion a trifling production of nitric acid in the air. A very minute quantity of nitric acid is also produced by the combustion of hydrogen and other substances in the atmosphere; it is also formed by the oxidation of ammonia.

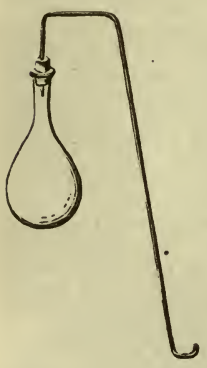
Nitric acid is not so easily detected in solution in small quantities as many other acids. Owing to the solubility of all its compounds, no *precipitant* can be found for this substance. An excellent mode of testing it is based upon its power of bleaching a solution of indigo in sulphuric acid when boiled with that liquid. The absence of chlorine must be insured in this experiment by means which will hereafter be described: otherwise the result is equivocal.

The best method for the detection of nitric acid is the following. The substance to be examined is boiled with a small quantity of water, and the solution cautiously mixed with an equal volume of concentrated sulphuric acid; the liquid is then allowed to cool, and a strong solution of ferrous sulphate carefully poured upon it, so as to form a separate layer. If large quantities of nitric acid are present, the surface of contact, first, and then the whole of the liquid, becomes black. If but small quantities of nitric acid are present, the liquid becomes reddish-brown or purple.

The ferrous sulphate reduces the nitric acid to nitrogen dioxide, which, dissolving in the solution of ferrous sulphate, imparts to it a dark color.

Nitrogen Monoxide (sometimes called *Nitrous Oxide;* also *Laughing-Gas*).— When solid ammonium nitrate is heated in a retort or flask,* fig. 116, furnished with a perforated cork and bent tube, it is resolved into water and nitrogen monoxide.†

Fig. 116.



No particular precaution is required in the operation, save due regulation of the heat, and the avoidance of tumultuous disengagement of the gas.

Nitrogen monoxide is a colorless, transparent, and almost inodorous gas, of distinctly sweet taste. Its specific gravity is 1·525; a litre of it weighs 0·97172 grams; 100 cubic inches weigh 47·29 grains. It supports the combustion of a taper or a piece of phosphorus with almost as much energy as pure oxygen: it is easily distinguished, however, from that gas by its solubility in cold water, which dissolves nearly its own volume: hence it is necessary to use tepid water in the pneumatic trough or gas-holder; otherwise great loss of gas will ensue. Nitrous oxide has been liquefied, but with difficulty: it requires, at 7·2° C. (45° F.), a pressure of 50 atmospheres: the liquid, when exposed under the bell-glass of the air-pump, is rapidly converted into a snow-like solid. When mixed with an equal volume of hydrogen, and fired by the electric spark in the eudiometer, it explodes with violence, and liberates its own measure of nitrogen. Every two volumes of the gas must consequently contain two volumes of nitrogen and one volume of oxygen, the whole being condensed or contracted one third — a constitution resembling that of vapor of water.

The most remarkable property of this gas is its intoxicating power upon the animal system. If quite pure, or merely mixed with atmospheric air, it may be respired for a short time without danger or inconvenience. The effect is very transient, and is not followed by depression.

Nitrogen Dioxide (sometimes called *Nitric Oxide*). — Clippings or turnings of copper are put into the apparatus employed for preparing hydrogen (p. 137), together with a little water, and nitric acid is added by the funnel until brisk effervescence is excited. The gas may be collected over cold water, as it is not sensibly soluble.

The reaction is a simple deoxidation of some of the nitric acid by the copper: the metal is oxidized, and the oxide so formed is dissolved by another portion of the acid. Nitric acid is very prone to act thus upon certain metals.‡

The gas obtained in this manner is colorless and transparent: in contact with air or oxygen gas it produces deep red fumes, which are readily absorbed by water: this character is sufficient to distinguish it from all other

* Florence oil-flasks, which may be purchased at a very trifling sum, constitute exceedingly useful vessels for chemical purposes, and often supersede retorts or other expensive apparatus. They are rendered still more valuable by cutting the neck smoothly round with a hot iron, softening it in the flame of a good Argand gas-lamp, and then turning over the edge so as to form a lip, or border. The neck will then bear a tightly fitting cork without risk of splitting.

† NO_3NH_4 (Ammonium nitrate.) = OH_2 (Water.) + N_2O (Nitrogen monoxide.)

‡ $8NO_3H$ (Nitric acid.) + Cu_3 (Copper.) = N_2O_2 (Nitrogen dioxide.) + $3(NO_3)_2Cu$ (Copper nitrate.) + $4H_2O$ (Water.)

gaseous bodies. A lighted taper plunged into the gas is extinguished; lighted phosphorus, however, burns in it with great brilliancy.

The specific gravity of nitrogen dioxide is 1·039; a litre weighs 1·34343 grams. It contains equal measures of oxygen and nitrogen gases united without condensation. When this gas is passed into the solution of a ferrous salt, it is absorbed in large quantity, and a deep-brown or nearly black liquid produced, which seems to be a definite compound of the two substances (p. 159). The compound is again decomposed by boiling.

Nitrogen Trioxide, or Nitrous Oxide. — When four measures of nitrogen dioxide are mixed with one measure of oxygen, and the gases, perfectly dry, are exposed to a temperature of —18°, they condense to a thin mobile blue liquid, which emits orange-red vapors.

Nitrous oxide, sufficiently pure for most purposes, is obtained by pouring concentrated nitric acid on lumps of arsenious acid, and gently warming the mixture, in order to start the reaction. Nitrous oxide is then evolved as an orange-red gas, arsenic acid remaining behind.

Nitrous oxide is decomposed by water, being converted into nitric acid and nitrogen dioxide.* For this reason it cannot be made to unite directly with metallic oxides; potassium nitrite may, however, be prepared by fusing potassium nitrate, whereby part of its oxygen is driven off; and many other salts of nitrous acid may be obtained by indirect means. Thus a solution of potassium or sodium nitrite may be prepared by passing the vapor of nitrogen trioxide, obtained as above by heating nitric acid with arsenious acid (or with starch), into a solution of caustic potash or soda.

Nitrogen Tetroxide (also called *Nitric Peroxide*). — This is the principal constituent of the deep-red fumes always produced when nitrogen dioxide escapes into the air.

When carefully dried lead nitrate is exposed to heat in a retort of hard glass, it is decomposed, lead oxide remaining behind, while a mixture of oxygen and nitrogen tetroxide is evolved. By surrounding the receiver with a very powerful freezing mixture, the latter is condensed in transparent crystals, or if the slightest trace of moisture is present, as a colorless liquid, which acquires a yellow and ultimately a red tint, as the temperature rises. At 27·8° it boils, giving off its well-known red vapor, the intensity of the color of which is greatly augmented by elevation of temperature. Its vapor is absorbed by strong nitric acid, which thereby acquires a yellow or red tint, passing into green, then into blue, and afterwards disappearing altogether on the addition of successive portions of water. The deep-red fuming acid of commerce, called *nitrous acid,* is simply nitric acid impregnated with nitrogen tetroxide.

Nitrogen tetroxide is decomposed by water at very low temperatures in such a manner as to yield nitric and nitrous acid; † but when added to excess of water at ordinary temperatures, it yields nitric acid, and the products of decomposition of nitrous acid, namely, nitric acid and nitrogen dioxide. In like manner, when passed into alkaline solutions, it forms a nitrate and a nitrite of the alkali-metal; but it has been also supposed to unite directly, under certain circumstances, with metallic oxides — lead oxide, for example — forming definite crystalline salts, and has hence been called *hyponitric acid;* but it is most probable that these salts are compounds of nitrates and nitrites.‡

* $3N_2O_3 + 0H_2 = 2NO_3H + 2N_2O_2$
Nitrogen trioxide. Water. Nitric acid. Nitrogen dioxide.

† $N_2O_4 + 0H_2 = NO_3H + NO_2H$
Nitrogen tetroxide. Water. Nitric acid. Nitrous acid.

‡ *E. g.*, $2(N_2O_4.PbO) = (NO_2)_2Pb + (NO_2)_2Pb$
Lead hyponitrate. Lead nitrate. Lead nitrite.

Nitrogen appears to combine, under favorable circumstances, with metals. When iron is heated to redness in an atmosphere of ammonia, it becomes brittle and crystalline, and shows an increase in weight, said to vary from 6 to 12 per cent.; while, according to other observers, the physical characters of the metal are changed without sensible alteration of weight. By heating copper in ammonia, no compound of nitrogen with copper is produced. But when ammonia is passed over copper oxide heated to 300°, water is formed, and a soft brown powder produced, which, when heated further, evolves nitrogen, and leaves metallic copper. The same effect is produced by the contact of strong acids. A similar compound of chromium with nitrogen appears to exist.

NITROGEN AND HYDROGEN; AMMONIA.

When powdered sal-ammoniac is mixed with moist calcium hydrate (slaked lime), and gently heated in a glass flask, a large quantity of gaseous matter is disengaged, which must be collected over mercury, or by displacement, advantage being taken of its low specific gravity.

Ammonia gas thus obtained is colorless; it has a strong pungent odor, and possesses in an eminent degree those properties to which the term *alkaline* is applied; that is to say, it turns the yellow color of turmeric to brown, that of reddened litmus to blue, and combines readily with acids, neutralizing them completely; by these reactions it is easily distinguished from all other bodies possessing the same physical characters. Under a pressure of 6·5 atmospheres at 15·5°, ammonia condenses to the liquid form.* Water dissolves about 700 times its volume of this gas, forming a solution which in a more dilute state has long been known under the name of *liquor ammoniæ;* by heat, a great part is again expelled † The solution is decomposed by chlorine, sal-ammoniac being formed, and nitrogen set free.

Ammonia has a density of 0·589; a litre weighs 0·76271 grams. It cannot be formed by the direct union of its elements, although it is sometimes produced under rather remarkable circumstances by the deoxidation of nitric acid.‡ The great sources of ammonia are the feebly compounded azotised principles of the animal and vegetable kingdoms, which, when left to putrefactive change, or subjected to destructive distillation, almost invariably give rise to an abundant production of this substance.

The analysis of ammonia gas is easily effected. When a portion is confined in a graduated tube over mercury, and electric sparks passed through it for a considerable time, the volume of the gas gradually increases until it becomes doubled. On examination, the tube is found to contain a mixture of 3 measures of hydrogen gas and 1 measure of nitrogen. Every two volumes of the ammonia, therefore, contained three volumes of hydrogen and one of nitrogen, the whole being condensed to the extent of one half. The weight of the two constituents is in the proportion of 3 parts hydrogen to 14 parts nitrogen.§

* [At the temperature of —75° F., liquid ammonia freezes into a colorless solid, heavier than the liquid itself.—(Faraday.) — R. B.]

† A concentrated solution of ammonia has recently been applied by M. Carré for producing intense cold (for the manufacture of ice). The apparatus used for this purpose consists of two strong iron cylinders connected by tubes, the one cylinder containing the solution of ammonia, the other being empty, and the whole apparatus being perfectly air-tight. The empty cylinder is now cooled with water, and the other cylinder is gently warmed. The ammonia escapes from the solution, and is condensed by its own pressure in the cooled cylinder. If the source of heat be now removed, the liquefied ammonia is again absorbed by the water, and the heat necessary for its transformation into vapor being taken from the iron vessel, the water surrounding it is converted into ice: by this process the temperature may be reduced to —15° C. (+ 5° F.)

‡ A mode of converting the nitrogen of the atmosphere into ammonia, by a succession of chemical operations, will be found under the head of Cyanogen.

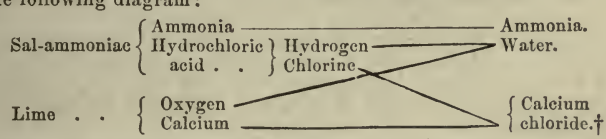
§ The formula of ammonia is NH_3.

Ammonia may also be decomposed into its elements by transmission through a red-hot tube.

Solution of ammonia is a very valuable reagent, and is employed in a great number of chemical operations, for some of which it is necessary to have it perfectly pure. The best mode of preparation is the following:

Equal weights of sal-ammoniac and quicklime are taken; the lime is slaked in a covered basin, and the salt reduced to powder. These are mixed and introduced into the flask employed in preparing solution of hydrochloric acid,* together with just enough water to damp the mixture, and cause it to aggregate into lumps; the rest of the apparatus is arranged exactly as in the former case, with an ounce or two of water in the wash-bottle, or enough to cover the ends of the tubes, and the gas conducted afterwards into pure distilled water, artificially cooled as before. The cork joints are made tight with wax; a little mercury is put into the safety-funnel, heat cautiously applied to the flask, and the whole left to itself. The disengagement of ammonia is very regular and uniform. Calcium chloride, with excess of calcium hydrate (slaked lime), remains in the flask.

The decomposition of the salt may be represented in the manner shown by the following diagram:



Solution of ammonia should be perfectly colorless, leave no residue on evaporation, and when supersaturated by nitric acid, give no cloud or muddiness with silver nitrate. Its density diminishes with its strength, that of the most concentrated being about 0·875; the value in alkali of any sample of liquor ammoniæ is most safely inferred, not from a knowledge of its density, but from the quantity of acid a given amount will saturate. The mode of conducting this experiment will be found described under *Alkalimetry*.

When solution of ammonia is mixed with acids of various kinds, salts are generated, which resemble in the most complete manner the corresponding potassium and sodium compounds: these are best discussed in connection with the latter.‡ Any ammoniacal salt can at once be recognized by the evolution of ammonia which takes place when it is heated with slaked lime, or solution of potash or soda.

CARBON.

This substance occurs in a state of purity, and crystallized, in two distinct and very dissimilar forms — namely, as diamond, and as graphite or plum-

* See fig. 132, p. 182.

† $2NH_4Cl$ (Sal-ammoniac.) + CaO (Lime) = $2NH_3$ (Ammonia.) + $CaCl_2$ (Calcium chloride.) + H_2O (Water.)

‡ The ammonia salts may be regarded either as direct compounds of ammonia, NH_3, with acids (HCl. for example), or as resulting from the replacement of the hydrogen of an acid by the group NH_4, called *ammonium*, which in this sense is a compound metal, chemically equivalent to potassium, sodium, silver, etc. Thus:

Ammonia hydrochlorate	$NH_3.HCl$	=	$NH_4.Cl$	Ammonium chloride.
" nitrate	$NH_3.HNO_3$	=	$NH_4.NO_3$	" nitrate.
" sulphate	$(NH_3)_2.H_2SO_4$	=	$(NH_4)_2.SO_4$	" sulphate.

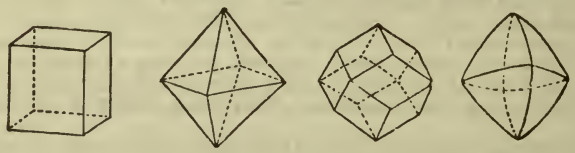
The formulæ in the second column are exactly analogous to those of the potassium salts, KCl, KNO_3, K_2SO_4.

bago. It constitutes a large proportion of all organic structures, animal and vegetable: when these latter are exposed to destructive distillation in close vessels, a great part of their carbon remains, obstinately retaining some of the hydrogen and oxygen, and associated with the earthy and alkaline matter of the tissue, giving rise to the many varieties of charcoal, coke, etc. This residue, when perfectly separated from all foreign matter, constitutes a third variety of carbon.

The diamond is one of the most remarkable substances known: long prized on account of its brilliancy as an ornamental gem, the discovery of its curious chemical nature confers upon it a high degree of scientific interest. Several localities in India, the island of Borneo, and more especially Brazil, furnish this beautiful substance. It is always distinctly crystallized, often quite transparent and colorless, but now and then having a shade of yellow, pink, or blue. The origin and true geological position of the diamond are unknown; it is always found embedded in gravel and transported materials whose history cannot be traced. The crystalline form of the diamond is that of the regular octohedron or cube, or some figure geometrically connected with these. Many of the octohedral crystals exhibit a very peculiar appearance, arising from the faces being curved or rounded, which gives to the crystal an almost spherical figure.

The diamond is infusible and unalterable even by a very intense heat, provided air be excluded; but when heated, thus protected, between the poles of a strong galvanic battery, it is converted into coke or graphite; heated to whiteness in a vessel of oxygen, it burns with facility, yielding carbonic acid gas.

Fig. 117.



The diamond is the hardest substance known: it admits of being split or cloven without difficulty in certain particular directions, but can only be cut or abraded by a second portion of the same material; the powder rubbed off in this process serves for polishing the new faces, and is also highly useful to the lapidary and seal-engraver. One very curious and useful application of the diamond is made by the glazier: a *fragment* of this mineral, like a bit of flint, or any other hard substance, scratches the surface of the glass; a *crystal* of diamond having the rounded octohedral figure spoken of, held in one particular position on the glass — namely, with an edge formed by the meeting of two adjacent faces presented to the surface — and then drawn along with gentle pressure, causes a split or cut, which penetrates to a considerable depth into the glass, and determines its fracture with perfect certainty.

Graphite or plumbago appears to consist essentially of pure carbon, although most specimens contain iron, the quantity of which varies from a mere trace up to five per cent. Graphite is a somewhat rare mineral: the finest and most valuable for pencils is brought from Borrowdale, in Cumberland, where a kind of irregular vein is found traversing the ancient slate beds of that district.* Crystals are not common: when they occur, they

* The graphite which can be directly cut for pencils occurring only in limited quantity, powdered graphite, obtained from the inferior varieties of the mineral, is now frequently consolidated for this purpose. The mechanical division of graphite presents considerable

have the figure of a short six-sided prism — a form bearing no geometric relation to that of the diamond.

Graphite is often formed artificially in certain metallurgic operations: the brilliant scales which sometimes separate from melted cast-iron on cooling, called by the workmen "kish," consist of graphite.

Lampblack, the soot produced by the imperfect combustion of oil or resin, is the best example that can be given of carbon in its uncrystallized or *amorphous* state. To the same class belong the different kinds of charcoal. That prepared from wood, either by distillation in a large iron retort, or by the smothered combustion of a pile of fagots partially covered with earth, is the most valuable as fuel. Coke, the charcoal of pit-coal, is much more impure; it contains a large quantity of earthy matter, and very often sulphur, the quality depending very much upon the mode of preparation. Charcoal from bones and animal matters in general is a very valuable substance, on account of the extraordinary power it possesses of removing coloring matters from organic solutions; it is used for this purpose by the sugar-refiners to a very great extent, and also by the manufacturing and scientific chemist. The property in question is possessed by all kinds of charcoal in a small degree.

Charcoal made from box, or other dense wood, has the property of condensing gases and vapors into its pores: of ammoniacal gas it is said to absorb not less than ninety times its volume, while of hydrogen it takes up less than twice its own bulk, the quantity being apparently connected with the property in the gas of suffering liquefaction. This property of absorbing gases, as well as the decolorizing power, no doubt depends in some way upon the same peculiar action of surface so remarkable in the case of platinum in a mixture of oxygen and hydrogen. The absorbing power is, indeed, considerably increased by saturating charcoal with solution of platinum, and subsequently igniting it, so as to coat the charcoal with a thin film of platinum. Dr. Stenhouse, who suggested this plan, finds that the gases thus absorbed undergo a kind of oxidation within the pores of the charcoal.*

Compounds of Carbon and Oxygen.

There are two direct inorganic compounds of carbon and oxygen

difficulties, which may be entirely obviated by adopting a chemical process suggested by Sir Benjamin Brodie, applicable, however, only to certain varieties, such as Ceylon graphite. This process consists in introducing the coarsely powdered graphite, previously mixed with $\frac{1}{4}$ of its weight of potassium chlorate, into 2 parts of concentrated sulphuric acid, which is heated in a water-bath until the evolution of acid fumes ceases. The acid is then removed by water, and the graphite dried. Thus prepared, this substance, when heated to a temperature approaching a red heat, swells up to a bulky mass of finely divided graphite. The graphite lately discovered in Siberia, which attracted such general attention at the Exhibition of 1862, likewise admits of being purified by Sir B. Brodie's process.

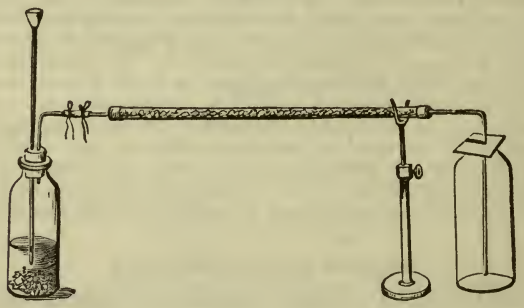
[* It removes from solution in water the vegetable bases, bitter principles, and astringent substances when employed in excess, requiring from twice to twenty times their weight for total precipitation. A solution of iodine in water, or of iodide of potassium, is quickly deprived of color. Metallic salts dissolved in water, or diluted alcohol, are precipitated, though not entirely, requiring about thirty times their weight of animal charcoal. Arsenious acid is totally carried out of solution. In these cases it acts in three different ways: the salt is absorbed unaltered; the oxide in the salt may be reduced; or, the salts precipitated in a basic condition, the solution showing an acid reaction as soon as the carbon begins to act. It is in this last case especially that traces of the bases can be detected, the acid set free preventing their total precipitation. The precipitation may hence be prevented by adding an excess of acid, and the bases after precipitation may be dissolved out by boiling with an acid solution.— Warrington, Mem Chim. Soc. 1845: Garrod, Pharm. Journ. 1845; Weppen, Ann. de Chim. 1845. Carbon is a combustible uniting with oxygen and producing carbonic acid. Its different forms exhibit much difference in this respect: In the very porous condition of charcoal it burns readily, while in its most dense form, the diamond, it requires a bright-red heat and pure oxygen gas. In the form of charcoal, it conducts heat slowly and electricity readily. Carbon is insoluble in water and not liable to be affected by air and moisture. It retards putrefaction. — R. B.]

called carbon monoxide and carbon dioxide: their composition may be thus stated:

	Composition by weight.	
	Carbon.	Oxygen.
Carbon monoxide . . .	12	16
Carbon dioxide . . .	12	32

Carbon Dioxide, or Carbonic Oxide (commonly called *Carbonic Acid*), is always produced when charcoal burns in air or oxygen gas: it is most conveniently obtained, however, for study, by decomposing a carbonate with one of the stronger acids. For this purpose, the apparatus for generating hydrogen may again be employed: Fragments of marble are put into the bottle with enough water to cover the extremity of the funnel-tube, and hydrochloric or nitric acid is added by the latter, until the gas is freely disengaged. Chalk-powder and dilute sulphuric acid may be used instead. The gas may be collected over water, although with some loss; or very conveniently by displacement, if it be required dry, as shown in fig. 118. The long drying-tube is filled with fragments of calcium chloride,

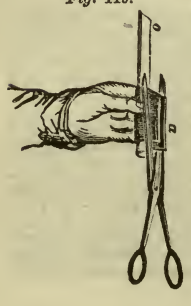
Fig. 118.



and the heavy gas is conducted to the bottom of the vessel in which it is to be received, the mouth of the latter being lightly closed.*

Carbon dioxide is a colorless gas; it has an agreeable pungent taste and color, but cannot be respired for a minute without insensibility following. Its specific gravity is 1·524,† a litre weighing 1·96664 grams and 100 cubic inches weighing 47·26 grains.

Fig. 119.



This gas is very hurtful to animal life, even when largely diluted with air; it acts as a nar-

* In connecting tube-apparatus for conveying gases or cold liquids, not corrosive, little tubes of caoutchouc about an inch long are *inexpressibly* useful. These are made by bending a piece of sheet india-rubber loosely round a glass tube or rod, and cutting off the superfluous portion with sharp scissors. The fresh-cut edges of the caoutchouc, pressed strongly together, cohere completely, and the tube is perfect, provided they have not been soiled by touching with the fingers. The connectors are secured by two or three turns of thin silk cord. Tubes of various sizes, made of vulcanized india-rubber, are now articles of commerce, and may be conveniently substituted for those made in the laboratory. The glass tubes are sold by weight, and are easily bent in the flame of a spirit-lamp, and, when necessary, cut by scratching with a file, and broken asunder.

† Dulong and Berzelius.

cotic poison. Hence the danger arising from imperfect ventilation, the use of fireplaces and stoves of all kinds unprovided with proper chimneys, and the crowding together of many individuals in houses and ships without efficient means for renewing the air; for carbon dioxide is constantly disengaged during the process of respiration, which, as we have seen (p. 131), is nothing but a process of slow combustion. This gas is sometimes emitted in large quantity from the earth in volcanic districts, and it is constantly generated where organic matter is in the act of undergoing fermentive decomposition. The fatal "after-damp" of the coal-mines contains a large proportion of carbon dioxide.

A lighted taper plunged into carbon dioxide is instantly extinguished even to the red-hot snuff. When diluted with three times its volume of air, it still retains the power of extinguishing a light. The gas is easily known from nitrogen, which is also incapable of supporting combustion, by its rapid absorption by caustic alkali, or by lime-water; the turbidity communicated to the latter from the production of insoluble calcium carbonate is very characteristic.

Cold water dissolves about its own volume of carbon dioxide, whatever be the density of the gas with which it is in contact (comp. p. 151); the solution temporarily reddens litmus-paper. In common soda-water, and also in effervescent wines, examples may be seen of the solubility of the gas. Even boiling water absorbs a perceptible quantity.

Some of the interesting phenomena attending the liquefaction of carbon dioxide have been already described: it requires for the purpose a pressure of between 27 and 28 atmospheres at 0°, according to Mr. Adams. The liquefied oxide is colorless and limpid, lighter than water, and four times more expansible than air: it mixes in all proportions with ether, alcohol, naphtha, oil of turpentine, and carbon disulphide, and is insoluble in water and fat oils. In this condition it does not exhibit any of the properties of an acid.

Carbon dioxide exists, as already mentioned, in the air: relatively its quantity is but small; but absolutely, taking into account the vast extent of the atmosphere, it is very great, and fully adequate to the purpose for which it is designed, — namely, to supply to plants their carbon, these latter having the power, by the aid of their green leaves, of decomposing carbon dioxide, retaining the carbon, and expelling the oxygen. The presence of light is essential to this effect, but of the manner in which it is produced we are yet ignorant.

The *carbonates* form a very large and important group of salts, some of which occur in nature in great quantities, as the carbonates of calcium and magnesium. They contain the elements of carbon dioxide and a metallic oxide: calcium carbonate, for example, being composed of 44 parts by weight of carbon dioxide and 56 parts of calcium oxide or lime, or of 12 carbon, 48 oxygen, and 40 calcium; * but they are never formed by the direct union of dry carbon dioxide with a dry metallic oxide, the intervention of water being always required to bring about the combination. Potassium carbonate (pearlash) is the chief constituent of wood-ashes; sodium carbonate is contained in the ashes of marine plants, and is manufactured on a very large scale by heating sodium sulphate with lime and coal. These carbonates are soluble in water. The other metallic carbonates, which are insoluble, may be formed by mixing a solution of potassium or sodium carbonate with a soluble metallic salt; thus, when solutions of lead nitrate and sodium carbonate are mixed together, the lead and sodium change places, forming sodium nitrate, which remains dissolved, and lead carbonate, which, being insoluble in water, is precipi-

* CO_3Ca or $CO_2.CaO$.

tated * in the form of a white powder. This is an example of *double decomposition*, the most frequent of all forms of chemical action.

The solution of carbon dioxide in water may be supposed to contain *hydrogen carbonate*, or *carbonic acid*, consisting of 12 parts by weight of carbon, 48 oxygen, and 2 hydrogen; † but this compound is not known in the separate state, only in aqueous solution.

Carbon Monoxide, or Carbonous Oxide (commonly called *Carbonic Oxide*). — When carbon dioxide is passed over red-hot charcoal or metallic iron, one-half of its oxygen is removed, and it becomes converted into carbon monoxide. A very good method of preparing this gas is to introduce into a flask fitted with a bent tube some crystallized oxalic acid, or salt of sorrel, and pour upon it five or six times as much strong oil of vitriol.‡ On heating the mixture, the organic acid is resolved into water, carbon dioxide, and carbon monoxide; and by passing the gases through a strong solution of caustic potash, the first is withdrawn by absorption, while the second remains unchanged. Another and, it may be, preferable method, is to heat finely powdered yellow potassium ferrocyanide with eight or ten times its weight of concentrated sulphuric acid. The salt is entirely decomposed, yielding a most copious supply of perfectly pure carbonous oxide gas, which may be collected over water in the usual manner.§

Carbon monoxide is a combustible gas; it burns with a beautiful pale-blue flame, generating carbon dioxide. It has never been liquefied. It is colorless, has very little odor, and is extremely poisonous — much more so than carbon dioxide. Mixed with oxygen, it explodes by the electric spark, but with some difficulty. Its specific gravity is 0·973; a litre weighs 1·2515 grams; 100 cubic inches weigh 30·21 grains.

The relation by volume of these oxides of carbon may thus be made intelligible: carbon dioxide contains its own volume of oxygen, that gas suffering no change of bulk by its conversion. One measure of carbon monoxide, mixed with half a measure of oxygen and exploded, yields one measure of carbon dioxide; hence carbon monoxide contains half its volume of oxygen.

Carbon monoxide unites with chlorine under the influence of light, forming a pungent, suffocating compound, possessing acid properties, called *phosgene gas*, or *carbonyl chloride*. It made by mixing equal volumes of carbon monoxide and chlorine, both perfectly dry, and exposing the mixture to sunshine: the gases unite quietly, the color disappears, and the volume becomes reduced to one half. A more convenient method for preparing this gas consists in passing carbon monoxide through antimony pentachloride. It is decomposed by water.

* CO_3Na_2 (Sodium carbonate.) + $(NO_3)_2Pb$ (Lead nitrate.) = $2NO_3Na$ (Sodium nitrate.) + CO_3Pb (Lead carbonate.)

† CO_3H_2 or CO_2OH_2.

‡ $2CO_4H_2$ (Oxalic acid.) = CO (Carbon monoxide.) + CO_2 (Carbon dioxide.) + OH_2 (Water.)

§ The reaction is represented by the equation:

$C_6N_6K_4Fe$ (Potassium ferrocyanide.) + $6OH_2$ (Water.) + $6SO_4H_2$ (Sulphuric acid.) = $6CO$ (Carbon monoxide.) + $2SO_4K_2$ (Potassium sulphate.) + $3SO_4(NH_4)_2$ (Ammonium sulphate.) + SO_4Fe (Ferrous sulphate.)

See a paper by the author in the Memoirs of the Chemical Society, i. 251.

Compounds of Carbon and Hydrogen.

The compounds of carbon and hydrogen already known are exceedingly numerous: perhaps all, in strictness, belong to the domain of organic chemistry, as they cannot, except in very few cases, be formed by the direct union of their elements, but always arise from the decomposition of a complex body of organic origin. It will be found convenient, notwithstanding, to describe two of them in this part of the volume, as they very well illustrate the important subjects of combustion and the nature of flame.

Methane or Marsh Gas; Light Carbonetted Hydrogen; Fire-damp.—This gas is but too often found to be abundantly disengaged in coal-mines from the fresh-cut surface of the coal, and from remarkable apertures or "blowers," which emit for a great length of time a copious stream or jet of gas, probably existing in a state of compression, pent up in the coal.

The mud at the bottom of pools in which water-plants grow, on being stirred, suffers bubbles of gas to escape, which may be easily collected. This, on examination, is found to be chiefly a mixture of light carbonetted hydrogen and carbon dioxide: the latter is easily absorbed by lime-water or caustic potash.

For a long time, no method was known by which the gas in question could be produced in a state approaching to purity by artificial means; the various illuminating gases from pit-coal and oil, and that obtained by passing the vapor of alcohol through a red-hot tube, contain large quantities of light carbonetted hydrogen, associated, however, with other substances which hardly admit of separation; but Dumas has discovered a method by which that gas can be produced at will; perfectly pure, and in any quantity.*

A mixture is made of 40 parts crystallized sodium acetate, 40 parts solid sodium hydrate, and 60 parts quicklime in powder. This mixture is transferred to a flask or retort, and strongly heated; the gas is disengaged in great abundance, and may be collected over water, while sodium carbonate remains behind.†

Methane is a colorless and nearly inodorous gas, which does not affect vegetable colors. It burns with a yellow flame, generating carbon dioxide and water. It is not poisonous, and may be respired to a great extent without apparent injury. The density of this compound is about 0·559, a litre weighing 0.71558 grams, and 100 cubic inches weighing 17·41 grains; it contains carbon and hydrogen associated in the proportion of 12 parts by weight of the former to 4 of the latter.‡

When 100 measures of this gas are mixed with 200 of pure oxygen in the eudiometer, and the mixture exploded by the electric spark, 100 measures of gas remain, which are entirely absorbable by a little solution of caustic potash. Now, carbon dioxide contains its own volume of oxygen: hence one-half the oxygen added — that is, 100 measures — must have been consumed in uniting with the hydrogen. Consequently, the gas must contain twice its own measure of hydrogen, and enough carbon to produce, when completely burned, an equal quantity of carbon dioxide.

* Ann. Chim. Phys. lxxiii. 93.

† The reaction is represented by the equation:

$C_2H_3O_2Na$	+	NaHO	=	CH_4	+	CO_3Na_2
Sodium acetate.		Sodium hydrate.		Marsh gas.		Sodium carbonate.

The use of the lime is merely to prevent the sodium hydrate from fusing and attacking the glass.

‡ The two carbides of hydrogen here described are represented by the following formula:

Methane or Marsh gas . . CH_4. Ethene or Olefiant gas . . C_2H_4.

When chlorine is mixed with marsh gas over water, no change follows, provided light be excluded. The presence of light, however, brings about decomposition, hydrochloric acid, carbon dioxide, and sometimes other products, being formed. It is important to remember that this gas is not acted upon by chlorine in the dark.

Ethene or Olefiant Gas. — Strong spirit of wine is mixed with five or six times its weight of oil of vitriol in a glass flask, the tube of which passes into a wash-bottle containing caustic potash. A second wash-bottle, partly filled with oil of vitriol, is connected with the first, and furnished with a tube dipping into the water of the pneumatic trough. On the first application of heat to the contents of the flask, alcohol, and afterwards ether, make their appearance; but, as the temperature rises, and the mixture blackens, the ether-vapor diminishes in quantity, and its place becomes in great part supplied by a permanent inflammable gas; carbon dioxide and sulphurous oxide are also generated at the same time, besides traces of other products. The two last-mentioned gases are absorbed by the alkali in the first bottle, and the ether-vapor by the acid in the second, so that the olefiant gas is delivered tolerably pure. The entire reaction is too complex to be discussed at the present moment; it will be found fully described in another part of the volume; but the ethene may be regarded as resulting from a simple dehydration of the alcohol by the oil of vitriol.* Olefiant gas thus produced is colorless, neutral, and but slightly soluble in water. Alcohol, ether, oil of turpentine, and even olive oil, as Faraday has observed, dissolve it to a considerable extent. It has a faint odor of garlic. On the approach of a kindled taper, it takes fire, and burns with a splendid white light, far surpassing in brilliancy that produced by marsh gas. This gas, when mixed with oxygen, and fired, explodes with extreme violence. Its density is 0·981; a litre weighs 1·25194 grams; 100 cubic inches weigh 30·57 grains.

By the use of the eudiometer, as already described, it has been found that each measure of ethene requires for complete combustion exactly three of oxygen, and produces under these circumstances two measures of carbon dioxide; whence it is evident that it contains twice its own volume of hydrogen combined with twice as much carbon as in methane.

By weight, these proportions will be 24 parts carbon and 4 parts hydrogen.

Ethene is decomposed by passing it through a tube heated to bright redness; a deposit of charcoal and tar takes place, and the gas becomes converted into marsh gas, or even into free hydrogen, if the temperature be very high. This latter change is, of course, attended by increase of volume.

Chlorine acts upon ethene in a very remarkable manner. When the two bodies are mixed, even in the dark, they combine in equal measures, and give rise to a heavy oily liquid, of sweetish taste and ethereal odor, to which the name of ethene chloride, or Dutch liquid,† is given. It is from this peculiarity that the term *olefiant* gas is derived.

A pleasing and instructive experiment may also be made by mixing in a tall jar two measures of chlorine and one of ethene, and then quickly applying a light to the mouth of the vessel. The chlorine and hydrogen unite with flame, which passes quickly down the jar, while the whole of the carbon is set free in the form of a thick black smoke.

Coal and Oil Gases. — The manufacture of coal-gas is, at the present moment, a branch of industry of great interest and importance in several points of view. The process is one of great simplicity of principle, but requires, in practice, some delicacy in management to yield a good result.

* C_2H_6O (Alcohol.) = C_2H_4 (Ethene.) + OH_2 (Water.)

† $C_2H_4Cl_2$

When pit-coal is subjected to destructive distillation, a variety of products show themselves — permanent gases, steam, and volatile oils, besides a not inconsiderable quantity of ammonia from the nitrogen always present in the coal. These substances vary very much in their proportions with the temperature at which the process is conducted, the permanent gases becoming more abundant with increased heat, but, at the same time, losing much of their value for the purposes of illumination.

The coal is distilled in cast-iron retorts, maintained at a bright-red heat, and the volatilized product is conducted into a long horizontal pipe of large dimensions, always half filled with liquid, into which the extremity of each separate tube dips: this is called the hydraulic main. The gas and its accompanying vapors are next made to traverse a refrigerator — usually a series of iron pipes, cooled on the outside by a stream of water; here the condensation of the tar and the ammoniacal liquid becomes complete, and the gas proceeds onward to another part of the apparatus, in which it is deprived of the sulphuretted hydrogen and carbonic acid gases always present in the crude product. This was formerly effected by slaked lime, which readily absorbs the compounds in question. The use of lime, however, has been almost superseded by that of a mixture of sawdust and iron oxide. This mixture, after having been employed, is exposed for some time to the atmosphere, and is then fit for use a second time. The purifiers are large iron vessels, filled either with slaked lime or with the iron oxide mixture. The gas is admitted at the bottom of the vessel, and made to pass over a large surface of the purifying agents. The last part of the operation, which, indeed, is often omitted, consists in passing the gas through dilute sulphuric acid, in order to remove ammonia. The quantity thus separated is very small, relatively, to the bulk of the gas, but, in an extensive work, becomes an object of importance.

Coal-gas thus manufactured and purified is preserved for use in immense cylindrical receivers, closed at the top, suspended in tanks of water by chains to which counterpoises are attached, so that the gas-holders rise and sink in the liquid as they become filled from the purifiers or emptied by the mains. These latter are made of large diameter, to diminish as much as possible the resistance experienced by the gas in passing through such a length of pipe. The joints of these mains are still made in so imperfect a manner that immense loss is experienced by leakage when the pressure upon the gas at the works exceeds that exerted by a column of water an inch in height.*

Coal-gas varies very much in composition, judging from its variable density and illuminating powers, and from the analyses which have been made. The difficulties of such investigations are very great, and unless particular precaution be taken, the results are merely approximative. The purified gas is believed to contain the following substances, of which the first is the most abundant, and the second the most valuable:

Methane, or Marsh gas.
Ethene, or Olefiant gas.
Hydrogen.

* It may give some idea of the extent of this species of manufacture, to mention that in the year 1838, for lighting London and the suburbs alone, there were eighteen public gas-works, and £2,800,000 invested in pipes and apparatus. The yearly revenue amounted to £450.000, and the consumption of coal in the same period to 180,000 tons, 1460 *millions* of cubic feet of gas being made in the year. There were 134,300 private lights, and 30,400 street lamps. 890 tons of coal were used in the retorts in the space of twenty-four hours at mid-winter, and 7,120,000 cubic feet of gas consumed in the longest night. — *Ure, Dictionary of Arts and Manufactures.*

Since that time, the production of gas has been enormously increased. The amount of coal used in London for gas-making in 1857 is estimated at more than 800,000 tons, yielding not less than 7,000,000 of cubic feet of gas. In the same year, the mains in the London streets had reached the extraordinary length of 2000 miles.

Carbon Monoxide.
Nitrogen.
Vapors of volatile liquid Hydrocarbons.*
Vapor of Carbon Bisulphide.

Separated by Condensation and by the Purifiers.

Tar and Volatile Oils.
Ammonium Sulphate, Chloride, and Sulphide.
Hydrogen Sulphide.
Carbon Dioxide.
Hydrocyanic acid, or Ammonium Cyanide.
Sulphocyanic acid, or Ammonium Sulphocyanate.

A far better illuminating gas may be prepared from oil, by dropping it into a red-hot iron retort filled with coke; the liquid is in great part decomposed and converted into permanent gas, which requires no purification, as it is quite free from the ammoniacal and sulphur compounds which vitiate gas from coal. Many years ago, this article was prepared in London; it was compressed for the use of the consumer into strong iron vessels, to the extent of 30 atmospheres; these were furnished with a screw-valve of peculiar construction, and exchanged for others when exhausted. The comparative high price of the material, and other circumstances, led to the abandonment of the undertaking. On the Continent, gas is now extensively prepared from wood.

COMBUSTION, AND THE STRUCTURE OF FLAME.

When any solid substance capable of bearing the fire is heated to a certain point, it emits light, the character of which depends upon the temperature. Thus, a bar of platinum or a piece of porcelain, raised to a particular temperature, becomes what is called red-hot, or emissive of red light: at a higher degree of heat, this light becomes whiter and more intense, and when urged to the utmost, as in the case of a piece of lime placed in the flame of the oxyhydrogen blowpipe, the light becomes exceedingly powerful, and acquires a tint of violet. Bodies in these states are said to be *incandescent* or *ignited.*

Again, if the same experiment be made on a piece of charcoal, similar effects will be observed; but something in addition: for whereas the platinum or porcelain, when removed from the fire, or the lime from the blowpipe flame, begin immediately to cool, and emit less and less light, until they become completely obscure, the charcoal maintains to a great extent its high temperature. Unlike the other bodies, too, which suffer no change whatever, either of weight or substance, the charcoal gradually wastes away until it disappears. This is what is called *combustion,* in contradistinction to mere ignition; the charcoal burns, and its temperature is kept up by the heat evolved in the act of union with the oxygen of the air.

In the most general sense, a body in a state of combustion is one in the act of undergoing intense chemical action: any chemical action whatsoever, if its energy rise sufficiently high, may produce the phenomenon of combustion, by *heating the body to such an extent that it becomes luminous.*

In all ordinary cases of combustion, the action lies between the burning body and the oxygen of the air; and since the materials employed for the economical production of heat and light consist of carbon chiefly, or that substance conjoined with a certain proportion of hydrogen and oxygen, all common effects of this nature are cases of the rapid and violent oxidation of carbon and hydrogen by the aid of the free oxygen of the air. The heat

* These bodies increase the illuminating power, and confer on the gas its peculiar odor.

must be referred to the act of chemical union, and the light to the elevated temperature.

By this principle, it is easy to understand the means which must be adopted to increase the heat of ordinary fires to the point necessary to melt refractory metals, and to bring about certain desired effects of chemical decomposition. .If the rate of consumption of the fuel can be increased by a more rapid introduction of air into the burning mass, the intensity of the heat will of necessity rise in the same ratio, the quantity of heat evolved being fixed and definite for the same constant quantity of chemical action. This increased supply of air may be effected by two distinct methods: it may be forced into the fire by bellows or blowing-machines, as in the common forge and in the blast and cupola-furnaces of the iron-worker, or it may be drawn through the burning materials by the help of a tall chimney, the fireplace being closed on all sides, and no entrance of air allowed, save between the bars of the grate. Such is the kind of furnace generally employed by the scientific chemist in assaying and in the reduction of metallic oxides by charcoal: the principle will be at once understood by the aid of the sectional drawing (fig. 120), in which a crucible is represented arranged in the fire for an operation of the kind mentioned.

Fig. 120.

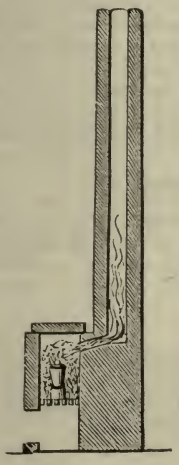
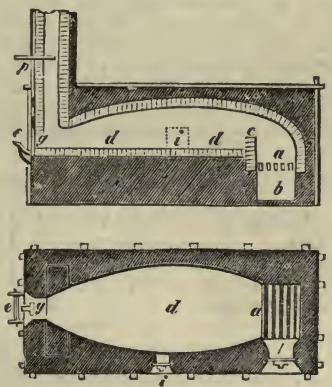


Fig. 121.



The "reverberatory" furnace (fig. 121) is one very much used in the arts when substances are to be exposed to heat without contact with the fuel. The fire-chamber is separated from the bed or hearth of the furnace by a low wall or *bridge* of brick-work, and the flame and heated air are reflected downward by the arched form of the roof. Any degree of heat can be obtained in a furnace of this kind — from the temperature of dull redness to that required to melt very large quantities of cast-iron. The fire is urged by a chimney provided with a sliding-plate, or damper, to regulate the draught.

Solids and liquids, as melted metal, possess, when sufficiently heated, the faculty of emitting light: the same power is exhibited by gaseous bodies, but the temperature required to render a gas luminous is incomparably higher than in the cases already described. Gas or vapor in this

condition constitutes *flame*, the actual temperature of which generally exceeds that of the white heat of solid bodies.

The light emitted from pure flame is often exceedingly feeble; but the illuminating power may be immensely increased by the presence of solid matter. The flame of hydrogen, or of the mixed gases, is scarcely visible in full daylight; in a dusty atmosphere, however, it becomes much more luminous by igniting to intense whiteness the floating particles with which it comes in contact. The piece of lime in the blow-pipe flame cannot have a higher temperature than that of the flame itself; yet the light it throws off is infinitely greater.

On the other hand, it is possible, as recently pointed out by Dr. Frankland, to produce very bright flames in which no solid particles are present. Metallic arsenic burnt in a stream of oxygen produces an intense white flame, although both the metal itself and the product of its combustion (arsenious oxide) are gaseous at the temperature of the flame. The combustion of a mixture of nitrogen dioxide and carbon bisulphide also produces a dazzling white flame, without any separation of solid matter.

The conditions most essential to luminosity in a flame are a high temperature, and the presence of gases or vapors of considerable density. The effect of high temperature is seen in the greater brightness of the flame of sulphur, phosphorus, and indeed all substances, when burnt in pure oxygen, as compared with that which results from their combustion in common air; in the former case the whole of the substances present take part in the combustion and generate heat, whereas in the latter the temperature is lowered by the presence of a large quantity of nitrogen, which contributes nothing to the effect. The relation between the luminosity of a flame and the vapor-densities of its constituents may be seen from the following table, in which the vapor-densities are referred to that of hydrogen as unity.

Relative Densities of Gases and Vapors.

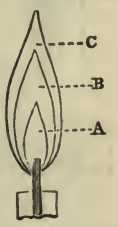
Hydrogen	1	Arsenious chloride	9¾
Water	9	Phosphoric oxide	71, or 142
Hydrochloric acid	18¼	Metallic arsenic	150
Carbon dioxide	22	Arsenious oxide	198
Sulphur dioxide	32		

A comparison of these numbers shows that the brightest flames are those which contain the densest vapors. Hydrogen burning in chlorine produces a vapor more than twice as heavy as that resulting from its combustion in oxygen, and accordingly the light produced in the former case is stronger than in the latter; carbon and sulphur burning in oxygen produce vapors of still greater density, namely, carbon dioxide and sulphur dioxide, and their combustion gives a still brighter light; lastly, phosphorus, which has a very dense vapor, and likewise yields a product of great vapor-density, burns in oxygen with a brilliancy which the eye can scarcely endure. Moreover, the luminosity of a flame is increased by condensing the surrounding gaseous atmosphere, and diminished by rarefying it. The flame of arsenic burning in oxygen may be rendered quite feeble by rarefying the oxygen; and on the contrary the faint flame of an ordinary spirit-lamp becomes very bright when placed under the receiver of a condensing pump. Frankland has also found that candles give much less light when burning on the top of Mont Blanc than in the valley below, although the rate of combustion in the two cases is nearly the same. The effect of condensation in increasing the brightness of a flame is also strikingly seen in the combustion of a mixture of oxygen and hydrogen, which gives but a feeble

light when burnt under the ordinary atmospheric pressure, as in the oxy-hydrogen blowpipe, but a very bright flash when exploded in the Cavendish eudiometer (p. 144), in which the water-vapor produced by the combustion is prevented from expanding.

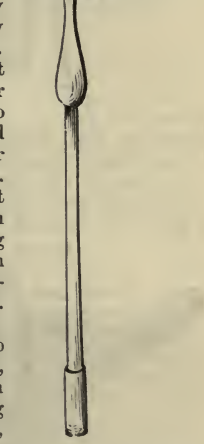
Flames burning in the air, and not supplied with oxygen from another source, are, as already stated, hollow, the chemical action being necessarily confined to the spot where the two bodies unite. That of a lamp or candle, when carefully examined, is seen to consist of three separate portions. The dark central part, easily rendered evident by depressing upon the flame a piece of fine wire-gauze, consists of combustible matter drawn up by the capillarity of the wick, and volatilized by the heat. This is surrounded by a highly luminous cone or envelope, which, in contact with a cold body, deposits soot. On the outside, a second cone is to be traced, feeble in its light-giving power, but having an exceedingly high temperature. The most probable explanation of these appearances is as follows: Carbon and hydrogen are very unequal in their attraction for oxygen, the latter greatly exceeding the former in this respect: consequently, when both are present, and the supply of oxygen limited, the hydrogen takes up the greater portion of the oxygen, to the exclusion of a great part of the carbon. Now, this happens, in the case under consideration, at some little distance within the outer surface of the flame — namely, in the luminous portion; the little oxygen which has penetrated thus far inward is mostly consumed by the hydrogen, and hydro-carbons are separated, rich in carbon and of great density in the state of vapor (naphthalene, chrysene, pyrene, etc.). These hydro-carbons, which would form smoke if they were cooler, and are deposited on a cold body held in the flame in the form of soot,* become intensely ignited by the burning hydrogen, and evolve a light whose whiteness marks a very elevated temperature. In the exterior and scarcely visible cone, these hydro-carbons undergo combustion.

Fig. 122.



A jet of coal-gas exhibits the same phenomena; but if the gas be previously mingled with air, or if air be forcibly mixed with, or driven into the flame, no such separation of carbon occurs; the hydrogen and carbon burn *together*, forming vapors of much lower density, and the illuminating power almost disappears.

Fig. 123.



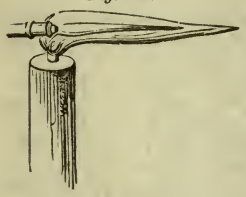
The common mouth blowpipe is a little instrument of great utility; it is merely a brass tube fitted with an ivory mouthpiece, and terminated by a jet having a small aperture, by which a current of air is driven across the flame of a candle. The best form is perhaps that contrived by Mr. Pepys, and shown in fig. 123. The flame so produced is very peculiar.

Instead of the double envelope just described, two long pointed cones are observed (fig. 124), which, when the blowpipe is good, and the aperture smooth and round, are very well defined, the outer cone being yellowish and the inner blue. A double combustion is, in fact, going on, by the blast in the inside, and by the external air. The space between the inner and outer cones is filled with exceedingly hot combustible matter, possessing strong reducing or deoxidizing powers; while the highly heated air just beyond the point of the exterior

* Soot is not pure carbon, but a mixture of heavy hydro-carbons.

cone oxidizes with great facility. A small portion of matter, supported on a piece of charcoal, or fixed in a ring at the end of a fine platinum wire, can thus in an instant be exposed to a very high degree of heat under these contrasted circumstances, and observations of great value made in a very short time. The use of the instrument requires an even and uninterrupted blast of some duration, by a method easily acquired with a little patience: it consists in employing for the purpose the muscles of the cheeks alone, respiration being conducted through the nostrils, and the mouth from time to time replenished with air, without intermission of the blast.

Fig. 124.



The Argand lamp, adapted to burn either oil or spirit, but especially the latter, is a very useful piece of chemical apparatus. In this lamp the wick is cylindrical, the flame being supplied with air both inside and outside: the combustion is greatly aided by the chimney, which is made of copper when the lamp is used as a source of heat.

Fig. 125 exhibits, in section, an excellent lamp of this kind for burning alcohol or wood-spirit. It is constructed of thin copper, and furnished with ground caps to the wick-holder and aperture,* by which the spirit is introduced, in order to prevent loss when the lamp is not in use. Glass spirit-lamps (fig. 126), fitted with caps to prevent evaporation, are very convenient for occasional use, being always ready and in order.†

Fig. 125.

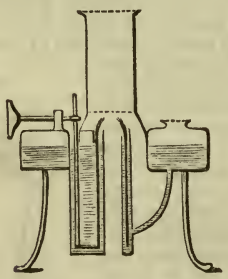
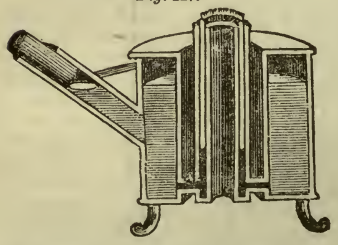


Fig. 126.

In London, and other large towns where coal-gas is to be had, it is constantly used with the greatest economy and advantage in every respect as a source of heat. Retorts, flasks, capsules, and other vessels, can be thus

Fig. 127.

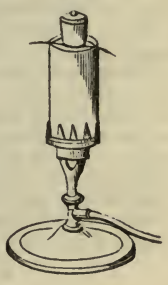


* When in use, this aperture must always be open, otherwise an accident is sure to happen; the heat expands the air in the lamp, and the spirit is forced out in a state of inflammation.

† [A modification of the Argand lamp contrived by the late Professor J. K. Mitchel is advantageous, from the wick-holder being kept constantly cool by the current of air always passing between it and the body of the lamp. "It is made of tinned iron. The alcohol is poured out by means of the hollow handle, and is admitted to the cylindrical burner by two or three tubes which are placed at the very bottom of the fountain. By such an arrangement of parts, the alcohol may be added as it is consumed, and the flame kept uniform; and as the pipes which pass to the burner are so remote from the flame, the alcohol never becomes heated so as to fly off through the vent-hole, and thus to cause greater waste and danger of explosion." R. B.]

exposed to an easily regulated and invariable temperature for many successive hours. Small platinum crucibles may be ignited to redness by placing them over the flame on a little wire triangle. The arrangement shown in fig. 127, consisting of a common Argand gas-burner fixed on a heavy and low foot, and connected with a flexible tube of caoutchouc or other material, is very convenient.

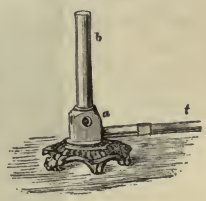
Fig. 128.



A higher temperature, and perfectly smokeless flame, is, however, obtained by burning the gas previously mixed with air. Such a flame is easily produced by placing a cap of wire-gauze on the chimney of the Argand burner just described, and setting fire to the gas above the wire-gauze. The flame does not penetrate below, but the gas in passing up the chimney becomes mixed with air, and this mixture burns above the cap with a blue, smokeless flame.

Another kind of burner for producing a smokeless flame has been contrived by Professor Bunsen, and is now very generally used in chemical laboratories. In this burner (fig. 129) the gas, supplied by a flexible tube, *t*, passes through a set of small holes into the box at *a*, in which it mixes with atmospheric air entering freely by a number of holes near the top of the box. The gaseous mixture passes up the tube *b*, and is inflamed at the top, where it burns with a tall, blue, smokeless flame, giving very little light, but much heat. By arranging two or more such tubes, together with an air-box containing a sufficient number of holes, a very powerful burner may be constructed.

Fig. 129.



Considerable improvements in this form of burner have been made by Mr. Griffin, who has also constructed, on the same principle, powerful gas-furnaces, affording heat sufficient for the decomposition of silicates, and the fusion of considerable quantities of copper or iron.* The principle of burning a mixture of gas and air is also applied in Hofmann's gas-furnace for organic analysis, which will be described under Organic Chemistry.

The kindling-point, or temperature at which combustion commences, is very different with different substances: phosphorus will sometimes take fire in the hand; sulphur requires a temperature exceeding that of boiling water; charcoal must be heated to redness. Among gaseous bodies the same fact is observed: hydrogen is inflamed by a red-hot wire; light carbonetted hydrogen requires a white heat to effect the same thing. When flame is cooled by any means below the temperature at which the rapid oxidation of the combustible gas occurs, it is at once extinguished. Upon this depends the principle of Sir H. Davy's invaluable safety-lamp.

Mention has already been made of the frequent disengagement of great quantities of light carbonetted hydrogen gas in coal-mines. This gas, mixed with seven or eight times its volume of atmospheric air, becomes highly explosive, taking fire at a light and burning with a pale-blue flame; and many fearful accidents have occurred from the ignition of large quantities of mixed gas and air occupying the extensive galleries and workings of a mine. Sir H. Davy undertook an investigation with a view to discover some remedy for this constantly occurring calamity: his labors resulted in some exceedingly important discoveries respecting flame, which led to the construction of the lamp which bears his name.

* See the article on Gas-burners and Furnaces in Watts's "Dictionary of Chemistry," ii. 782.

When two vessels filled with a gaseous explosive mixture are connected by a narrow tube, and the contents of one fired by the electric spark, or otherwise, the flame is not communicated to the other, provided the diameter of the tube, its length, and the conducting power for heat of its material, bear a certain proportion to each other; the flame is extinguished by cooling, and its transmission rendered impossible.

In this experiment, high conducting power and diminished diameter compensate for diminution in length; and to such an extent can this be carried, that metallic gauze, which may be looked upon as a series of very short square tubes arranged side by side, when of sufficient degree of fineness, arrests in the most complete manner the passage of flame in explosive mixtures depending upon the inflammability of the gas. Now the fire-damp mixture has an exceedingly high kindling-point; a red heat does not cause inflammation; consequently, the gauze will be safe for this substance, when flame would pass in almost any other case.

The miner's safety lamp is merely an ordinary oil-lamp, the flame of which is enclosed in a cage of wire-gauze, made double at the upper part,

Fig. 130.

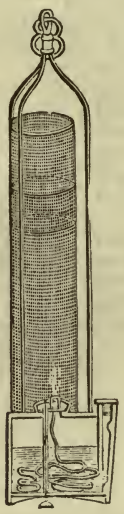
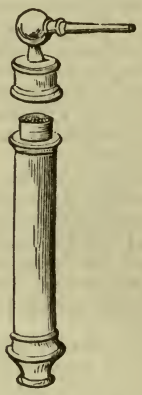


Fig. 131.



containing about 400 apertures to the square inch. The tube for supplying oil to the reservoir reaches nearly to the bottom of the latter, while the wick admits of being trimmed by a bent wire passing with friction through a small tube in the body of the lamp; the flame can thus be kept burning for any length of time, without the necessity of unscrewing the cage. When this lamp is taken into an explosive atmosphere, although the fire-damp may burn within the cage with such energy as sometimes to heat the metallic tissue to dull redness, the flame is not communicated to the mixture on the outside.

These effects may be conveniently studied by suspending the lamp in a large glass jar, and gradually admitting coal-gas below. The oil-flame is at first elongated, and then, as the proportion of gas increases, extinguished, while the interior of the gauze cylinder becomes filled with the burning mixture of gas and air. As the atmosphere becomes purer, the wick is once more relighted. These appearances are so remarkable that

the lamp becomes an admirable indicator of the state of the air in different parts of the mine.*

The same great principle has been ingeniously applied by Mr. Hemming to the construction of the oxy-hydrogen safety-jet before mentioned. This is a tube of brass about four inches long, filled with straight pieces of fine brass wire, the whole being tightly wedged together by a pointed rod, forcibly driven into the centre of the bundle, (fig. 131.) The arrangement thus presents a series of metallic tubes, very long in proportion to their diameter, the cooling powers of which are so great as to prevent the possibility of the passage of flame, even with oxygen and hydrogen. The jet may be used, as before mentioned, with a common bladder, without a chance of explosion. The fundamental fact of flame being extinguished by contact with a cold body, may be elegantly shown by twisting a copper wire into a short spiral, about 0·1 inch in diameter, and then passing it *cold* over the flame of a wax candle; the latter is extinguished. If the spiral be now heated to redness by a spirit-lamp, and the experiment repeated, no such effect follows.

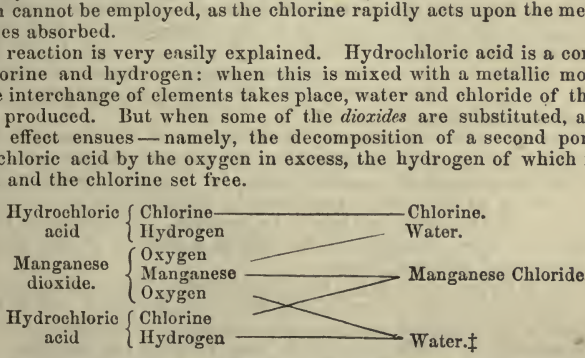
CHLORINE.

This substance is a member of a very important natural group, containing also iodine, bromine, and fluorine. So great a degree of resemblance exists between these bodies in all their chemical relations, especially between chlorine, bromine, and iodine, that the history of one will almost serve, with a few little alterations, for that of the rest.

Chlorine† is a very abundant substance: in common salt it exists in combination with sodium. It is most easily prepared by pouring strong hydrochloric acid upon finely powdered black oxide of manganese contained in a retort or flask, and applying a gentle heat; a heavy yellow gas is disengaged, which is the substance in question.

It may be collected over warm water, or by displacement: the mercurial trough cannot be employed, as the chlorine rapidly acts upon the metal, and becomes absorbed.

The reaction is very easily explained. Hydrochloric acid is a compound of chlorine and hydrogen: when this is mixed with a metallic monoxide, double interchange of elements takes place, water and chloride of the metal being produced. But when some of the *dioxides* are substituted, an additional effect ensues — namely, the decomposition of a second portion of hydrochloric acid by the oxygen in excess, the hydrogen of which is withdrawn and the chlorine set free.



* This is the true use of the lamp — namely, to permit the viewer or superintendent, without risk to himself, to examine the state of the air in every part of the mine; not to enable workmen to continue their labors in an atmosphere habitually explosive, which must be unfit for human respiration, although the evil effects may be slow to appear. Owners of coal-mines should be compelled either to adopt efficient means of ventilation, or to close workings of this dangerous character altogether.

† From χλωρός, yellowish-green, the name given to it by Sir H. Davy.

‡ $MnO_2 + 4HCl = Cl_2 + MnCl_2 + 2OH_2$

Manganese dioxide. Hydrochloric acid. Chlorine. Manganese chloride. Water.

Chlorine was discovered by Scheele in 1774, but its nature was long misunderstood. It is a yellow gaseous body, of intolerably suffocating properties, producing very violent cough and irritation when inhaled even in exceedingly small quantity. It is soluble to a considerable extent in water, that liquid absorbing at 15·5° (60° F.), about twice its volume, and acquiring the color and odor of the gas. When this solution is exposed to light, it is slowly changed, by decomposition of water, into hydrochloric acid, the oxygen being at the same time liberated. When moist chlorine gas is exposed to a cold of 0°, yellow crystals are formed, which consist of a definite compound of chlorine and water, containing 35·5 parts of the former to 90 of the latter.

Fig. 132.

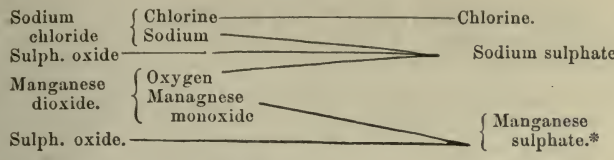
Chlorine has a specific gravity of 2·47; a litre of it weighs 3·17344 grams; exposed to a pressure of about four atmospheres, it condenses to a yellow limpid liquid.

Chlorine has but little attraction for oxygen, its chemical energies being principally exerted towards hydrogen and the metals. A lighted taper plunged into the gas, continues to burn with a dull-red light, and emits a large quantity of smoke, the hydrogen of the wax being alone consumed, and the carbon separated. If a piece of paper be wetted with oil of turpentine, and thrust into a bottle filled with chlorine, the chemical action of the latter upon the hydrogen is so violent as to cause inflammation, accompanied by a copious deposit of soot. Although chlorine can, by indirect means, be made to combine with carbon, yet this never occurs under the circumstances described.

Phosphorus takes fire spontaneously in chlorine, burning with a pale and feebly luminous flame. Several of the metals, as copper leaf, powdered antimony, and arsenic, undergo combustion in the same manner. A mixture of equal measures of chlorine and hydrogen explodes with violence on the passage of an electric spark, or on the application of a lighted taper, hydrochloric acid gas being formed. Such a mixture may be retained in the dark for any length of time without change: exposed to diffuse daylight, the two gases slowly unite, while the direct rays of the sun induce instantaneous explosion.

The most characteristic property of chlorine is its bleaching power; the most stable organic coloring principles are instantly decomposed and destroyed by this remarkable agent: indigo, for example, which resists the action of strong oil of vitriol, is converted by chlorine into a brownish substance, to which the blue color cannot be restored. The presence of water is essential to these changes, for the gas in a state of perfect dryness is incapable even of affecting litmus.

Chlorine is largely used in the arts for bleaching linen and cotton goods, rags for the manufacture of paper, &c. For these purposes, it is employed, sometimes in the state of gas, sometimes in that of solution in water, but more frequently in combination with lime, forming the substance called bleaching-powder. When required in large quantities, it is often made by pouring slightly diluted oil of vitriol upon a mixture of common salt and manganese oxide contained in a large leaden vessel. The decomposition which ensues may be thus represented:

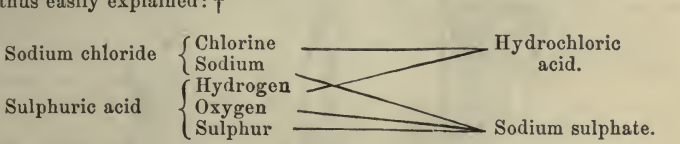


Chlorine is one of the best and most potent substances that can be used for the purpose of disinfection, but its employment requires care. Bleaching-powder mixed with water, and exposed to the air in shallow vessels, becomes slowly decomposed by the carbonic acid of the atmosphere, and the chlorine is evolved: if a more rapid disengagement be wished, a little acid of any kind may be added. In the absence of bleaching-powder, either of the methods for the production of the gas described may be had recourse to, always taking care to avoid an excess of acid.

Hydrogen Chloride; Hydrochloric, Chlorhydric, or Muriatic Acid.—This substance, in a state of solution in water, has been long known. The gas is prepared with the utmost ease by heating in a flask fitted with a cork and bent tube, a mixture of common salt and oil of vitriol diluted with a small quantity of water; it must be collected by displacement, or over mercury. It is a colorless gas, which fumes strongly in the air from condensing the atmospheric moisture; it has an acid, suffocating odor, but is much less offensive than chlorine. Exposed to a pressure of 40 atmospheres, it liquefies.

Hydrochloric acid gas has a density of 1·269 compared with air, or 18·25 compared with hydrogen as unity. It is exceedingly soluble in water, that liquid taking up at the temperature of the air about 418 times its bulk. The gas and solution are powerfully acid.

The action of oil of vitriol on common salt, or any analogous substance, is thus easily explained: †



The composition of this substance may be determined by synthesis: when a measure of chlorine and a measure of hydrogen are fired by the electric spark, two measures of hydrochloric acid gas result, the combination being unattended by change of volume. By weight it contains 35·5 parts of chlorine and 1 part of hydrogen.

Solution of hydrochloric acid, the liquid acid of commerce, is a very important preparation, and of extensive use in chemical pursuits: it is best prepared by the following arrangement: —

A large glass flask, containing a quantity of common salt, is fitted with a cork and bent tube, in the manner represented in fig. 132: this tube passes through and below a second short tube into a wide-necked bottle, containing a little water, into which the open tube dips. A bent tube is adapted to another hole in the cork of the wash-bottle, so as to convey the purified gas

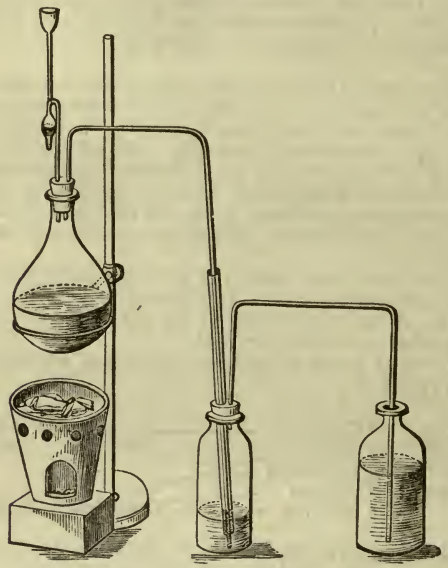
* $2NaCl + MnO_2 + 2SO_4H_2 = Cl_2 + SO_4Na_2 + SO_4Mn + 2OH_2$
Sodium chloride. Manganese dioxide. Hydrogen sulphate. Chlorine. Sodium sulphate. Manganous sulphate. Water.

† $2NaCl + SO_4H_2 = 2HCl + SO_4Na_2$
Sodium chloride. Hydrogen sulphate. Hydrogen chloride. Sodium sulphate.

into a quantity of distilled water, by which it is instantly absorbed: the joints are made air-tight by melting a little yellow wax over the corks.

A quantity of oil of vitriol, about equal in weight to the salt, is then slowly introduced by the funnel; the disengaged gas is at first wholly absorbed by the water in the wash-bottle, but when this becomes saturated, it passes into the second vessel and there dissolves. When all the acid has been added, heat may be applied to the flask by a charcoal chauffer, until its contents appear nearly dry, and the evolution of gas almost ceases, when the process may be stopped. As much heat is given out during the condensation of the gas, it is necessary to surround the condensing vessel with cold water.

Fig. 133.



The simple wash-bottle, shown in the last figure, will be found an exceedingly useful contrivance in a great number of chemical operations. It serves in the present, and in many similar cases, to retain any liquid or solid matter mechanically carried over with the gas, and it may be always employed when a gas of any kind is to be passed through an alkaline or other solution. The open tube dipping into the liquid prevents the possibility of absorption, by which a partial vacuum would be occasioned, and the liquid of the second vessel lost by being driven into the first.

The arrangement by which the acid is introduced also deserves a moment's notice. The tube is bent twice upon itself, and a bulb blown in one portion: the liquid poured into the funnel rises upon the opposite side of the first bend until it reaches the second; it then flows over and runs into the flask. Any quantity can then be got into the latter without the introduction of air, and without the escape of gas from the interior. The funnel acts also as a kind of safety-valve, and in both directions; for if by any chance the delivery-tube should be stopped, and the issue of gas prevented, its in-

creased elastic force soon drives the little column of liquid out of the tube, the gas escapes, and the vessel is saved. On the other hand, any absorption within is quickly compensated by the entrance of air through the liquid in the bulb.

Fig. 134.

The plan employed on the large scale by the manufacturer is the same in principle as that described; he merely substitutes a large iron cylinder, or apparatus made of lead, for the flask, and vessels of stoneware for those of glass.

On distilling an aqueous solution of hydrochloric acid, an acid is produced boiling at 110° (230° F.) which contains 20·22 per cent. of anhydrous hydrochloric acid: a more concentrated solution when heated gives off hydrochloric acid gas; a weaker solution loses water. Roscoe and Dittmar have proved that the composition of the distillate varies with the atmospheric pressure; it cannot, therefore, be viewed as a chemical compound.

Pure solution of hydrochloric acid is transparent and colorless: when strong, it fumes in the air by evolving a little gas. It leaves no residue on evaporation, and gives no precipitate or opacity with diluted solution of barium chloride. When saturated with the gas, it has a specific gravity of 1·21, and contains about 42 per cent. of real acid. The commercial acid, which is obtained in immense quantity as a secondary product in the manufacture of sodium sulphate by the action of sulphuric acid upon common salt, has usually a yellow color, and is very impure, containing salts, sulphuric acid, chloride of iron, and organic matter. It may be rendered sufficiently pure for most purposes by diluting it to the density of 1·1, which happens when the strong acid is mixed with its own bulk or rather less of water, and then distilling it in a retort furnished with a Liebig's condenser.

A mixture of nitric and hydrochloric acids has long been known under the name of *aqua regia*, from its property of dissolving gold. When these two substances are heated together, they both undergo decomposition, nitrogen tetroxide and chlorine being evolved. This, at least, appears to be the final result of the action: at a certain stage, however, two peculiar substances, consisting of nitrogen, oxygen, and chlorine (chloronitric acid gas* and chloronitrous gas †), appear to be formed. It is only the chlorine which attacks the metal.

The presence of hydrochloric acid, or any other soluble chloride, is easily detected by solution of silver nitrate. A white curdy precipitate is produced, insoluble in nitric acid, freely soluble in ammonia, and subject to blacken by exposure to light.

Oxides and Oxacids of Chlorine.

There are four oxacids of chlorine, which may be regarded as oxides of hydrochloric acid; thus:

	Composition by weight.‡				
	Chlorine.		Hydrogen.		Oxygen.
Hydrochloric acid . . .	35·5	+	1		
Hypochlorous acid	35·5	+	1	+	16
Chlorous acid	35·5	+	1	+	32
Chloric acid	35·5	+	1	+	48
Perchloric acid	35·5	+	1	+	64

* $NOCl_2$. † NOCl.

‡ Hypochlorous acid . . . . . ClHO
Chlorous acid . . . . . $ClHO_2$
Chloric acid . . . . . $ClHO_3$
Perchloric acid . . . . . $ClHO_4$.

The anhydrous chlorine oxides corresponding to hypochlorous and chlorous acids are known, namely: *—

	Chlorine.		Chlorine.		Oxygen.
Chlorine monoxide, or Hypochlorous oxide . .	35·5	+	35·5	+	16
Chlorine trioxide, or Chlorous oxide	35·5	+	35·5	+	48

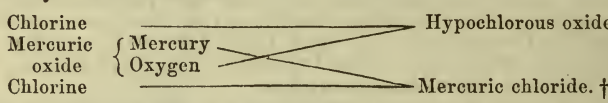
Also an oxide to which there is no corresponding acid, namely: —

	Chlorine.		Oxygen.
Chlorine tetroxide	2 × 35·5	+	64

The oxides corresponding to chloric and perchloric acid have not been obtained.

Hypochlorous and chloric acids are produced by the action of chlorine on certain metallic oxides in presence of water; hypochlorous and chlorous acids also by direct oxidation of hydrochloric acid. Perchloric acid and chlorine tetroxide result from the decomposition of chloric acid.

Hypochlorous Oxide, Acid, and Salts. — The oxide is best prepared by the action of chlorine gas upon dry mercuric oxide. This oxide, prepared by precipitation, and dried by exposure to a strong heat, is introduced into a glass tube kept cool and well washed, dry chlorine gas is slowly passed over it. Mercuric chloride and hypochlorous oxide are thereby formed; the latter is collected by displacement. The reaction by which it is produced may be thus illustrated:



The mercuric chloride, however, does not remain as such; it combines with another portion of the oxide when the latter is in excess, forming a peculiar brown compound, an oxychloride of mercury. It is remarkable that the *crystalline* mercuric oxide prepared by calcining the nitrate, or by the direct oxidation of the metal, is scarcely acted upon by chlorine under the circumstances described.

Hypochlorous oxide is a pale-yellow gaseous body, containing, in every two measures, two measures of chlorine and one of oxygen, and is therefore analogous in constitution to water. It explodes, although with no great violence, by slight elevation of temperature. Its odor is peculiar, and quite different from that of chlorine. When the flask or bottle in which the gas is received is exposed to artificial cold by the aid of a mixture of ice and salt, the hypochlorous oxide condenses to a deep-red liquid, slowly soluble in water, and very subject to explosion.‡

Hypochlorous acid is produced by the solution of hypochlorous oxide in water; also by passing air saturated with hydrochloric acid gas through a solution of potassium permanganate acidulated with hydrochloric acid and heated in a water bath: the distillate is a solution of hypochlorous acid, formed by oxidation of the hydrochloric acid; thirdly, by decomposing a metallic hypochlorite with sulphuric acid or other oxacid; fourthly, by passing chlorine gas into water holding in suspension a solution containing metallic oxides, hydrates, carbonates, sulphates, phosphates, &c., the most

* Chlorine monoxide or Hypochlorous oxide . . . . . Cl_2O
Chlorine trioxide or Chlorous oxide . . . . . Cl_2O_3
Chlorine tetroxide . . . . . Cl_2O_4.

† $2HgO$ (Mercuric oxide.) + Cl_4 (Chlorine.) = $HgCl_2{\cdot}HgO$ (Mercuric oxychloride.) + Cl_2O (Hypochlorous oxide.)

‡ Pelouze Ann. Chim. Phys. [3], vii. 112.

advantageous for the purpose being mercuric oxide, or calcium carbonate (chalk).*

The aqueous solution of hypochlorous acid has a yellowish color, an acid taste, and a characteristic sweetish smell. The strong acid decomposes rapidly even when kept in ice. The dilute acid is more stable, but is decomposed by long boiling into chloric acid, water, chlorine, and oxygen. Hydrochloric acid decomposes it, with formation of chlorine.† It is a very powerful bleaching and oxidizing agent, converting many of the elements — iodine, selenium, and arsenic, for example — into their highest oxides, and at the same time liberating chlorine.

Metallic hypochlorites may be obtained in the pure state by neutralizing hypochlorous acid with metallic hydrates, such as those of sodium, calcium, copper, &c.; but they are usually prepared by passing chlorine gas into solutions of alkalies or alkaline carbonates, or over the dry hydrates of the earth-metals — dry slaked lime, for example. In this process a metallic chloride is formed at the same time.‡ The salts thus obtained constitute the bleaching and disinfecting salts of commerce. They will be more fully described under the head of calcium salts.

Chlorous Oxide, Acid, and Salts. — The oxide is prepared by heating in a flask filled to the neck, a mixture of 4 parts of potassium chlorate and 3 parts of arsenious acid, or oxide, with 12 parts of nitric acid previously diluted with 4 parts of water. During the operation, which must be performed in a water-bath, a greenish-yellow gas is evolved, which is permanent in a freezing mixture of ice and salt, but liquefiable by extreme cold. It dissolves freely in water and in alkaline solutions, forming chlorous acid and metallic chlorites. The reaction by which chlorous oxide is formed is somewhat complicated. The arsenious acid deprives the nitric acid of part of its oxygen, reducing it to nitrous acid, which is then reoxidized at the expense of the chloric acid, reducing it to chlorous oxide.§

Chlorous Acid may be prepared by condensing chlorous oxide in water, or by decomposing a metallic chlorite with dilute sulphuric or phosphoric acid. Its concentrated solution is a greenish-yellow liquid having strong bleaching and oxidizing properties. It does not decompose carbonates, but acts strongly with caustic alkalies and earths to form chlorites.

Chlorine Tetroxide. — When potassium chlorate is made into a paste with concentrated sulphuric acid, and cooled, and this paste is very cautiously heated by warm water in a small glass retort, a deep-yellow gas is evolved, which is the body in question; it can be collected only by displacement, since mercury decomposes and water absorbs it.

Chlorine tetroxide has a powerful odor, quite different from that of the preceding compounds, and of chlorine itself. It is exceedingly explosive, being resolved with violence into its elements by a temperature short of the boiling-point of water. Its preparation is, therefore, always attended with danger, and should be performed only on a small scale. It is composed by measure of one volume of chlorine and two volumes of oxygen,

* CO_3Ca + OH_2 + Cl_4 = CO_2 + $CaCl_2$ + $2ClHO$
Calcium carbonate. Water. Chlorine. Carbon dioxide. Calcium chloride. Hypochlorous acid.

† $ClHO$ + ClH = O_2H = Cl_2.

‡ CaH_2O_2 + Cl_4 = $CaCl_2O_2$ + $CaCl_2$ + OH_2
Calcium hydrate. Chlorine. Calcium hypochlorite. Calcium chloride. Water.

§ $2ClO_3H$ + $2NO_2H$ = $2NO_3H$ + OH_2 + Cl_2O_3
Chloric acid. Nitrous acid. Nitric acid. Water. Chlorous oxide.

condensed into two volumes.* It may be liquefied by cold. The solution of the gas in water bleaches.

The *euchlorine* of Davy, prepared by gently heating potassium chlorate with dilute hydrochloric acid, is probably a mixture of chlorous acid and free chlorine.

The production of chlorine tetroxide from potassium chlorate and sulphuric acid depends upon the spontaneous splitting of the chloric acid into chlorine tetroxide and perchloric acid, which latter remains as a potassium salt.†

When a mixture of potassium chlorate and sugar is touched with a drop of oil of vitriol, it is instantly set on fire, the chlorine tetroxide disengaged being decomposed by the combustible substance with such violence as to cause inflammation. If crystals of potassium chlorate be thrown into a glass of water, a few small fragments of phosphorus added, and then oil of vitriol poured down a narrow funnel reaching to the bottom of the glass, the phosphorus will burn beneath the surface of the water, by the assistance of the oxygen of the chlorine tetroxide disengaged. The liquid at the same time becomes yellow, and acquires the odor of that gas.

Chloric Acid. — This is the most important compound of the series. When chlorine is passed to saturation into a moderately strong hot solution of potassium hydrate or carbonate, and the liquid concentrated by evaporation, it yields, on cooling, flat tabular crystals of a colorless salt, consisting of potassium chlorate. The mother-liquor contains potassium chloride.‡

From potassium chlorate, chloric acid may be obtained by boiling the salt with a solution of hydrofluosilicic acid, which forms an almost insoluble potassium salt, decanting the clear liquid, and digesting it with a little silica, which removes the excess of the hydrofluosilicic acid. Filtration through paper must be avoided.

By cautious evaporation, the acid may be so far concentrated as to assume a sirupy consistence; it is then very easily decomposed. It sometimes sets fire to paper, or other dry organic matter, in consequence of the facility with which it is deoxidized by combustible bodies.

The chlorates are easily recognized; they give no precipitate when in solution with silver nitrate; they evolve pure oxygen when heated, passing thereby into chlorides; and they afford, when treated with sulphuric acid, the characteristic explosive yellow gas already described. The dilute solution of the acid has no bleaching power.

Perchloric Acid. — When powdered potassium chlorate is thrown by small portions at a time into hot nitric acid, a change takes place of the same description as that which happens when sulphuric acid is used, but with this important difference: that the chlorine and oxygen, instead of being evolved in a dangerous state of combination, are emitted in a state of *mixture*. The result of the reaction is a mixture of potassium nitrate and perchlorate, which may be readily separated by their difference of solubility.

Perchloric acid is obtained by distilling potassium perchlorate with sulphuric acid. Pure perchloric acid is a colorless liquid, of 1·782 sp. gr. at 15·5° (60° F.), not solidifying at —35° (—31° F.); it soon becomes colored

* Its formula is Cl_2O_4.

† $6ClO_3K$ (Potassium chlorate.) + $3SO_4H_2$ (Hydrogen sulphate.) = $2Cl_2O_4$ (Chlorine tetroxide.) + $2ClO_4H$ (Hydrogen perchlorate.) + $3SO_4K_2$ (Potassium sulphate.) + $2H_2O$ (Water.)

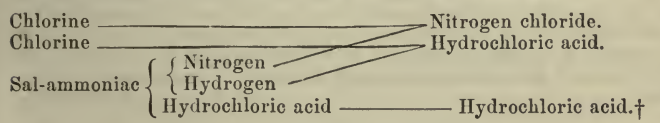
‡ $3K_2O$ (Potassium oxide.) + Cl_6 (Chlorine.) = $5KCl$ (Potassium chloride.) + ClO_3K (Potassium chlorate.)

even if kept in the dark, and after a few weeks decomposes with explosion. The vapor of perchloric acid is transparent and colorless: in contact with moist air, it produces dense white fumes. The acid, when cautiously mixed with a small quantity of water, solidifies to a crystalline mass, which is a compound of perchloric acid with one molecule of water.* When brought in contact with carbon, ether, or other organic substances, perchloric acid explodes with nearly as much violence as chloride of nitrogen.

Compound of Chlorine and Nitrogen. — When sal-ammoniac or ammonia nitrate is dissolved in water, and a jar of chlorine inverted in the solution, the gas is absorbed, and a deep-yellow oily liquid is observed to collect upon the surface of the solution, ultimately sinking in globules to the bottom. This is nitrogen chloride, the most dangerously explosive substance known. The following is the safest method of conducting the experiment: —

A somewhat dilute and tepid solution of pure sal-ammoniac in distilled water poured into a clean basin, and a bottle of chlorine, the neck of which is quite free from grease, inverted into it. A shallow and heavy leaden cup is placed beneath the mouth of the bottle to collect the product. When enough has been obtained, the leaden vessel may be withdrawn with its dangerous contents, the chloride remaining covered with a stratum of water. The operator should protect his face with a strong wire-gauze mask when experimenting upon this substance.

The change may be explained by the following diagram: —



Nitrogen chloride is very volatile, and its vapor is exceedingly irritating to the eyes. It has a specific gravity of 1·653. It may be distilled at 71° (160° F.), although the experiment is attended with great danger. Between 93° (200° F.) and 105° (221° F.) it explodes with the most fearful violence. Contact with almost any combustible matter, as oil or fat of any kind, determines the explosion at common temperatures; a vessel of porcelain, glass, or even of cast-iron, is broken to pieces, and the leaden cup receives a deep indentation. This body has usually been supposed to contain nitrogen and chlorine in the proportion of 14 parts of the former to 106·5 parts of the latter, but recent experiments upon the corresponding iodine compound (p. 191) induce a belief that it contains hydrogen.‡

Chlorine and Carbon. — Several compounds of chlorine and carbon are known.§ They are obtained indirectly by the action of chlorine upon certain organic compounds, and will be described under Organic Chemistry.

* $ClO_4H + OH_2$.

† NH_4Cl + $6Cl$ = NCl_3 + $4HCl$
Ammonium chloride. Chlorine Nitrogen trichloride. Hydrochloric acid.

‡ Instead of NCl_3, it may in reality be $NHCl_2$, or NH_2Cl.

§ C_2Cl_2, C_2Cl_4, C_2Cl_6, and CCl_4.

BROMINE.

Bromine* was discovered by Balard in 1826. It is found in sea-water, and is a frequent constituent of saline springs, chiefly as magnesium bromide: a celebrated spring of the kind exists near Kreuznach in Prussia. Bromine may be obtained pure by the following process, which depends upon the fact that ether, agitated with an aqueous solution of bromine, removes the greater part of that substance.

The mother-liquor, from which the less soluble salts have separated by crystallization, is exposed to a stream of chlorine, and then shaken up with ether; the chlorine decomposes the magnesium bromide, and the ether dissolves the bromine thus set free. On standing, the ethereal solution, having a fine red color, separates, and may be removed by a funnel or pipette. Caustic potash is then added in excess, and heat applied; potassium bromide and bromate are formed. The solution is evaporated to dryness, and the saline matter, after ignition to redness to decompose the bromate, is heated in a small retort with manganese dioxide and sulphuric acid diluted with a little water, the neck of the retort being plunged into cold water. The bromine volatilizes in the form of a deep-red vapor, which condenses into drops beneath the liquid.

Bromine is at common temperatures a red thin liquid of an exceedingly intense color, and very volatile; it freezes at about —7° (19° F.), and boils at 63° (143° F.) The density of the liquid is 2·976, and that of the vapor 5·54 compared with air, and 80 compared with hydrogen. The odor of bromine is very suffocating and offensive, much resembling that of iodine, but more disagreeable. It is slightly soluble in water, more freely in alcohol, and most abundantly in ether. The aqueous solution bleaches.

Hydrogen Bromide, or Hydrobromic Acid.† — This substance bears the closest resemblance to hydriodic acid: it has the same constitution by volume, very nearly the same properties, and may be prepared by means exactly similar, substituting the one body for the other (see page 189). The solution of hydrobromic acid has also the power of dissolving a large quantity of bromine, thereby acquiring a red tint. Hydrobromic acid contains by weight 80 parts bromine and 1 part hydrogen.

Bromic Acid.‡ — Caustic alkalis in presence of bromine undergo the same change as with chlorine, a metallic bromide and bromate being produced: these may often be separated by the inferior solubility of the latter. Bromic acid, obtained from barium bromate, closely resembles chloric acid; it is easily decomposed. The bromates, when heated, lose oxygen and become bromides.

A hypobromous acid corresponding to hypochlorous acid is likewise known.

IODINE.

This element was first noticed in 1812 by M. Courtois, of Paris. Minute traces are found in combination with sodium or potassium in sea-water, and occasionally a much larger proportion in that of certain mineral springs. It seems to be in some way beneficial to many marine plants, as

* From *βρῶμος*, a noisome smell: a very appropriate term.

† HBr. ‡ BrO_3H.

these latter have the power of abstracting it from the surrounding water, and accumulating it in their tissues. It is from this source that all the iodine of commerce is derived. It has lately been found in minute quantity in some aluminous slates of Sweden, and in several varieties of coal and turf.

Kelp, or the half-vitrified ashes of sea-weeds, prepared by the inhabitants of the Western Islands and the northern shores of Scotland and Ireland, is treated with water, and the solution filtered. The liquid is then concentrated by evaporation until it is reduced to a very small volume, the sodium chloride, sodium carbonate, potassium chloride, and other salts being removed as they successively crystallize. The dark-brown mother-liquor left contains very nearly the whole of the iodine, as iodide of sodium, magnesium, &c.: this is mixed with sulphuric acid and manganese dioxide, and gently heated in a leaden retort, when the iodine distils over and condenses in the receiver. The theory of the operation is exactly analogous to that of the preparation of chlorine; in practice, however, it requires careful management, otherwise the impurities present in the solution interfere with the general result.*

The manganese is not absolutely necessary; potassium or sodium iodide, heated with an excess of sulphuric acid, evolves iodine. This effect is due to a secondary action between the hydriodic acid first produced and the excess of the sulphuric acid, in which both suffer decomposition, yielding iodine water, and sulphurous acid.

Iodine crystallizes in plates or scales of a bluish-black color and imperfect metallic lustre, resembling that of plumbago: the crystals are sometimes very large and brilliant. Its density is 4·948. It melts at 107° (225° F.), and boils at 175° (347° F.), the vapor having an exceedingly beautiful violet color.† It is slowly volatile, however, at common temperatures, and exhales an odor much resembling that of chlorine. The density of the vapor is 8·716 compared with air, 127 compared with hydrogen. Iodine requires for solution about 7000 parts of water, which nevertheless acquires a brown color; in alcohol it is much more freely soluble. Solutions of hydriodic acid and the iodides of the alkaline metals also dissolve a large quantity: these solutions are not decomposed by water, which is the case with the alcoholic tincture

Iodine stains the skin, but not permanently; it has a very energetic action upon the animal system, and is much used in medicine.

One of the most characteristic properties of iodine is the production of a splendid blue color by contact with starch. The iodine for this purpose must be free or uncombined. It is easy, however, to make the test available for the purpose of recognizing the presence of the element in question when a soluble iodide is suspected; it is only necessary to add a very small quantity of chlorine-water, when the iodine, being displaced from combination, becomes capable of acting upon the starch.

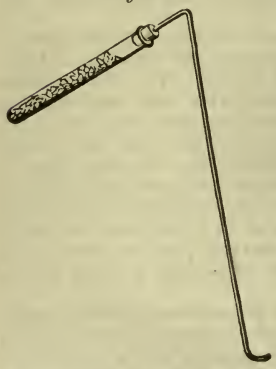
Hydrogen Iodide, or Hydriodic Acid. — The simplest process for preparing hydriodic acid gas is to introduce into a glass tube, sealed at one extremity, a little iodine, then a small quantity of roughly powdered glass moistened with water, upon this a few fragments of phosphorus, and lastly more glass: this order of iodine, glass, phosphorus, glass, is repeated until the tube is half or two-thirds filled. A cork and narrow bent tube are then fitted, and gentle heat applied. The gas is best collected by displacement of air. The experiment depends on the formation of an iodide of

* $2KI$	+	MnO_2	+	$2SO_4H_2$	=	I_2	+	SO_4K_2	+	SO_4Mn	+	$2OH_2$
Potassium iodide.		Manganese dioxide.		Hydrogen sulphate		Iodine.		Potassium sulphate.		Manganese sulphate.		Water.

† Whence the name, from ἰωδής, violet-colored.

phosphorus and its subsequent decomposition by water, whereby hydrogen phosphite, or phosphorous acid, and hydrogen iodide are produced.* The glass merely serves to moderate the violence of the action of the iodine upon the phosphorus.

Fig. 135.



Hydriodic acid gas greatly resembles the corresponding chlorine compound; it is colorless, and highly acid; it fumes in the air, and is very soluble in water. Its density is about 4·4 compared with air, 64 compared with hydrogen. By weight, it is composed of 127 parts iodine and 1 part hydrogen; and by measure of equal volumes of iodine vapor and hydrogen united without condensation.

Solution of hydriodic acid may be prepared by a process much less troublesome than the above. Iodine in fine powder is suspended in water, and a stream of washed hydrogen sulphide passed through the mixture; sulphur is deposited, and the iodine converted into hydriodic acid. When the liquid has become colorless, it is heated, to expel the excess of hydrogen sulphide, and filtered. The solution cannot be kept long, especially if it be concentrated; the oxygen of the air gradually decomposes the hydriodic acid, and iodine is set free, which, dissolving in the remainder, communicates to it a brown color.

Compounds of Iodine and Oxygen.

The most important of these are the iodic and periodic oxides.

	Composition by weight.†	
	Iodine.	Oxygen.
Iodic oxide	127	40
Periodic oxide	127	56

Both these are acid oxides, uniting with water and metallic oxides, and forming salts called iodates and periodates. The composition of the hydrogen salts is as follows: ‡—

	Iodine.	Oxygen.	Hydrogen.		Iodic oxide.		Water.
Hydrogen Iodate or Iodic acid	127	+ 48	+ 1	or	334	+	18
Hydrogen Periodate or Periodic acid	127	+ 56	+ 1	or	386	+	18

Iodic acid may be prepared by the direct oxidation of iodine with nitric acid of specific gravity 1·5; 5 parts of dry iodine with 200 parts of nitric acid are kept at a boiling temperature for several hours, or until the iodine has disappeared. The solution is then cautiously distilled to dryness, and the residue dissolved in water and made to crystallize.

Iodic acid is a very soluble substance; it crystallizes in colorless, six-sided tables. At 107° (224° F.) it is resolved into water and iodic oxide, which forms tabular rhombic crystals, and when heated to the temperature of boiling olive oil, is completely resolved into iodine and oxygen. The solution of iodic acid is readily deoxidized by sulphurous acid. The iodates

* P_2 + I_6 + $6OH_2$ = $6HI$ + $2PO_3H_3$
Phosphorus. Iodine. Water. Hydrogen iodide. Hydrogen phosphite.

† I_2O_5 and I_2O_7.

‡ $I_2O_5.OH_2$ = $2IO_3H$; $I_2O_7.OH_2$ = $2IO_4H$.

much resemble the chlorates: that of potassium is decomposed by heat into potassium iodide and oxygen gas.

Periodic Acid. — When solution of sodium iodate is mixed with caustic soda, and a current of chlorine transmitted through the liquid, two salts are formed — namely, sodium chloride and a compound of sodium periodate with sodium hydrate, which is sparingly soluble.* This is separated, converted into a silver-salt, and dissolved in nitric acid: the solution yields, on evaporation, crystals of yellow silver periodate, from which the acid may be separated by the action of water, which resolves the salt into free acid and insoluble basic periodate.

Periodic acid crystallizes from its aqueous solution in deliquescent oblique rhombic prisms, which melt at 130° (266° F.), and are resolved at 170° (338° F.) into water and a white mass of periodic oxide, which at 180° or 190° (356°—374° F.) gives off oxygen with great rapidity, and leaves iodic oxide.

The solution of periodic acid is reduced by many organic substances, and instantly by hydrochloric acid, sulphurous acid, and hydrogen sulphide. With hydrochloric acid it forms water, iodine chloride, and free chlorine. The metallic periodates are resolved by heat into oxygen and metallic iodide.

Compounds of Iodine and Nitrogen. — When finely powdered iodine is put into caustic ammonia, it is in part dissolved, giving a deep-brown solution, and the residue is converted into a black powder, called *nitrogen iodide.*† The brown liquid consists of hydriodic acid, holding iodine in solution, and is easily separated from the solid product by a filter. The latter, while still wet, is distributed in small quantities upon separate pieces of bibulous paper, and left to dry in the air.

Nitrogen iodide is a black insoluble powder, which, when dry, explodes with the slightest touch — even that of a feather — and sometimes without any obvious cause. The explosion is, however, not nearly so violent as that of nitrogen chloride, and is attended with the production of violet fumes of iodine. According to Dr. Gladstone, this substance contains hydrogen, and may be viewed as ammonia in which two thirds of the hydrogen are replaced by iodine.‡ According to the researches of Bunsen, it must be viewed as a combination of nitrogen tri-iodide with ammonia.§ It appears, however, that the substance called nitrogen iodide varies in composition. Gladstone, by changing the mode of preparation, obtained several compounds of nitrogen tri-iodide with ammonia.

Compounds of Iodine and Chlorine. — Iodine readily absorbs chlorine gas, forming, when the chlorine is in excess, a solid yellow compound, and when the iodine preponderates, a brown liquid. The solid iodide is decomposed by water, yielding hydrochloric and iodic acids. ‖

Another definite compound is formed by heating in a retort a mixture of 1 part iodine and 4 parts potassium chlorate; oxygen gas and iodine chloride are disengaged, and the latter may be condensed by suitable means. Potassium iodate and perchlorate remain in the retort.

This iodine chloride is a yellow oily liquid, of suffocating smell and astringent taste; it is soluble in water and alcohol without decomposition. It probably consists of 127 parts iodine and 35·5 parts chlorine.¶

* IO_3Na + $3NaHO$ + Cl_2 = $2Na.Cl$ + $IO_6H_3Na_2$
Sodium iodate. Sodium hydrate. Chlorine Sodium chloride. Basic sodium periodate.

† NI_3. ‡ NHI_2. § $NI_3.NH_3$.

‖ Hence it is doubtless ICl_5. ¶ ICl.

FLUORINE.

This element has never been isolated — at least, in a state fit for examination; its properties are consequently in great measure unknown; but from the observations made, it is presumed to be gaseous, and to possess color, like chlorine. The compounds containing fluorine can be easily decomposed, and the element transferred from one body to another; but its intense chemical energies towards the metals and towards silicium, a component of glass, have hitherto baffled all attempts to obtain it pure in the separate state. As calcium fluoride, it exists in small quantities in many animal substances, such as bones. Several chemists have endeavored to obtain it by decomposing silver fluoride by means of chlorine in vessels of fluor-spar, but even these experiments have not led to a decisive result.

Hydrogen Fluoride, or Hydrofluoric Acid.*— When powdered calcium fluoride (fluor-spar) is heated with concentrated sulphuric acid in a retort of platinum or lead connected with a carefully cooled receiver of the same metal, a very volatile colorless liquid is obtained, which emits copious white and highly suffocating fumes in the air. This was formerly believed to be the acid in the anhydrous state. Louyet, however, states that it still contains water, and that hydrofluoric acid, like hydrochloric acid, when anhydrous, is a gas. The anhydrous acid may be prepared, according to Frémy, by distilling hydrogen and potassium fluoride in a platinum vessel. The acid is gaseous at ordinary temperatures. In a frigorific mixture it exists as a liquid, which acts violently on water and evolves white fumes.

When hydrofluoric acid is put into water, it unites with the latter with great violence: the dilute solution attacks glass with great facility. The concentrated acid, dropped upon the skin, occasions deep and malignant ulcers, so that great care is requisite in its management. Hydrofluoric acid contains 19 parts fluorine and 1 part hydrogen.

In a diluted state, this acid is occasionally used in the analysis of siliceous minerals, when alkali is to be estimated: it is employed, also, for etching on glass, for which purpose the acid may be prepared in vessels of lead, that metal being but slowly attacked under these circumstances. The vapor of the acid is also very advantageously applied to the same object in the following manner: The glass to be engraved is coated with etching-ground or wax, and the design traced in the usual way with a pointed instrument. A shallow basin made by beating up a piece of sheet-lead is then prepared, a little powdered fluor-spar placed in it, and enough sulphuric acid added to form with the latter a thin paste. The glass is placed upon the basin, with the waxed side downward, and gentle heat applied beneath, which speedily disengages the vapor of hydrofluoric acid. In a very few minutes, the operation is complete: the glass is then removed and cleaned by a little warm oil of turpentine. When the experiment is successful, the lines are very clean and smooth.

No combination of fluorine and oxygen has yet been discovered.

* HF.

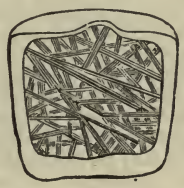
SULPHUR.

This is an elementary body of great importance and interest. It is often found in the free state in connection with deposits of gypsum and rock-salt; its occurrence in volcanic districts is probably accidental. Sicily furnishes a large proportion of the sulphur employed in Europe. In a state of combination with iron and other metals, and as sulphuric acid united to lime and magnesia, it is also abundant.

Pure sulphur is a pale-yellow brittle solid, of well-known appearance. It melts when heated, and distils over unaltered, if air be excluded. The crystals of sulphur exhibit two distinct and incompatible forms — namely, first, an octohedron with rhombic base (fig. 136), which is the figure of native sulphur, and that assumed when sulphur separates from solution at common temperatures, as when a solution of sulphur in carbon bisulphide is exposed to slow evaporation in the air; and, secondly, a lengthened prism having no relation to the preceding: this happens when a mass of sulphur is melted, and, after partial cooling, the crust on the surface is broken and the fluid portion poured out. Fig. 137 shows the result of such an experiment.

Fig. 136.

Fig. 137.



The specific gravity of sulphur varies according to the form in which it is crystallized. The octohedral variety has the specific gravity 2·045; the prismatic variety the specific gravity 1·982.

Sulphur melts at 111° (232° F.) (at 114·5°, according to Brodie): at this temperature it is of the color of amber, and thin and fluid as water; when further heated, it begins to thicken, and to acquire a deeper color; and between 221° (430° F.) and 249° (480° F.) it is so tenacious that the vessel in which it is contained may be inverted for a moment without the loss of its contents. If in this state it be poured into water, it retains for many hours a remarkably soft and flexible condition, which should be looked upon as the amorphous state of sulphur. After a while it again becomes brittle and crystalline. From the temperature last mentioned to the boiling-point — about 400° (792° F.) — sulphur again becomes thin and liquid. In the preparation of commercial flowers of sulphur, the vapor is conducted into a large cold chamber, where it condenses in minute crystals. The specific gravity of sulphur vapor is 2·22, referred to that of air as unity, or 32 compared with that of hydrogen (Deville).

Sulphur is insoluble in water and alcohol; oil of turpentine and the fat oils dissolve it, but the best substance for the purpose is carbon bisulphide. In its chemical relations sulphur bears great resemblance to oxygen: to very many oxides there are corresponding sulphides, and the sulphides often unite among themselves, forming crystallizable compounds analogous to oxysalts.

Sulphur is remarkable for the great number of modifications which it is capable of assuming. Of these, however, there are two principal well-characterized varieties, one soluble, and the other insoluble in carbon bisulphide, and many minor modifications. The soluble variety is distinguished by Berthelot* by the name of *electro-negative sulphur*, because it is the form which appears at the positive pole of the voltaic battery during the decomposition of an aqueous solution of hydrogen sulphide, and is separated from the combinations of sulphur with the electro-positive metals. The insoluble variety is distinguished as *electro-positive sulphur*, because it is the form which appears at the negative pole during the electric decomposition of sulphurous acid, and separates from compounds of sulphur with the electro-negative elements, chlorine, bromine, oxygen, &c.

The principal modifications of soluble sulphur are the octohedral and prismatic varieties already mentioned, and an amorphous variety which is precipitated as a greenish-white emulsion, known as milk of sulphur on adding an acid to a dilute solution of an alkaline polysulphide, such, for example, as is obtained by boiling sulphur with milk of lime.† This amorphous sulphur changes by keeping into a mass of minute octohedral crystals. Sublimed sulphur appears also to be allied to this modification, but it always contains a small portion of one of the insoluble modifications.

The chief modifications of insoluble sulphur are: 1. The amorphous insoluble variety, obtained as a soft magma by decomposing chlorine bisulphide with water, or by adding dilute hydrochloric acid to the solution of a hyposulphite.‡ 2. The plastic sulphur already mentioned as obtained by pouring viscid melted sulphur into water. A very similar variety is produced by boiling metallic sulphides with nitric or nitro-muriatic acid.

Magnus § obtained a black modification of sulphur by repeatedly heating sulphur to 300° (572° F.), cooling suddenly, and exhausting with carbon bisulphide; and this black sulphur, heated to a temperature between 130° and 150°, passed into a red modification. According to Mitscherlich, however, pure sulphur does not exhibit these modifications; but various highly colored products may be obtained by melting sulphur with small quantities of fatty matters. Even the grease imparted by touching sulphur with the fingers is sufficient to alter its color considerably when melted.

When solutions of hydrogen sulphide and ferric chloride are mixed together, a blue precipitate is sometimes formed, which is said to be a peculiar modification of sulphur.

Compounds of Sulphur and Oxygen.

There are two oxides of sulphur whose names and composition are as follows:

	Composition by weight.		
	Sulphur.		Oxygen.
Sulphur dioxide or Sulphurous oxide . . .	32	+	32
Sulphur trioxide or Sulphuric oxide . . .	32	+	48

Both these oxides unite with water and metallic oxides, or the elements thereof, producing salts; those derived from sulphurous oxide are called

* Ann. Chim Phys. [3], xlix. 430.

† CaS_5 + $2HCl$ = $CaCl_2$ + SH_2 + S_4
Calcium pentasulphide. + Hydrochloric acid. = Calcium chloride. + Hydrogen sulphide. + Sulphur.

‡ $2Cl_2S_2$ + $3OH_2$ = $4HCl$ + $S_2O_3H_2$ + S_2
Chlorine bisulphide. + Water. = Hydrochloric acid. + Hyposulphurous acid. + Sulphur,

§ Poggendorff's Annalen, xcii. 308.

sulphites, and those derived from sulphuric acid, sulphates. The composition of the hydrogen salts, or acids, is as follows: *

	Sulphur.		Oxygen.		Hydrogen.		Sulphurous oxide.		Water.
Hydrogen Sulphite, or Sulphurous acid	32	+	48	+	2	=	64	+	18
							Sulphuric oxide.		Water.
Hydrogen Sulphate, or Sulphuric acid	32	+	64	+	2	=	80	+	18

The replacement of half or the whole of the hydrogen in these acids, by metals, gives rise to metallic sulphites and sulphates.

There are also several acids of sulphur, with their corresponding metallic salts, to which there are no corresponding anhydrous oxides, viz.:

1. *Hyposulphurous* or *Thiosulphuric Acid*, having the composition of sulphuric acid in which one fourth of the oxygen is replaced by sulphur.† Its composition by weight is:

Sulphur.		Oxygen.		Hydrogen.
64	+	48	+	2

2. A series of acids called *Polythionic Acids*,‡ in which the same quantities of oxygen and hydrogen are united with quantities of sulphur in the proportion of the numbers 2, 3, 4, 5,§ viz.:

	Sulphur.		Oxygen.		Hydrogen.
Dithionic, or Hyposulphuric acid	64	+	96	+	2
Trithionic acid	96	+	96	+	2
Tetrathionic acid	128	+	96	+	2
Pentathionic acid	160	+	96	+	2

Sulphur Dioxide, or Sulphurous Oxide. — This is the only product of the combustion of sulphur in dry air or oxygen gas. It is most conveniently prepared by heating sulphuric acid with metallic mercury or copper clippings; a portion of the acid is decomposed, one third of the oxygen of the sulphuric oxide being transferred to the metal, while the sulphuric oxide is reduced to sulphurous oxide which escapes as gas.‖ Another very simple method of preparing sulphurous oxide consists in heating concentrated sulphuric acid with sulphur; a very regular evolution of sulphurous oxide is thus obtained. Sulphurous oxide is a colorless gas, having the peculiar suffocating odor of burning brimstone; it instantly extinguishes flame, and is quite irrespirible. Its density is 2·21; a litre weighs 2·8605 grams; 100 cubic inches weigh 68·69 grains. At —17·8° (0° F.), under the ordinary pressure of the atmosphere, this gas condenses to a colorless, limpid liquid, very expansible by heat. Cold water dissolves more than thirty times its volume of sulphurous oxide. The solution, which contains hydrogen sulphite or sulphurous acid, may be kept unchanged so long as air is excluded, but access of oxygen gradually converts the sulphurous into sulphuric acid, although dry sulphurous oxide and oxygen gases may remain in contact

* The composition of these oxides and acids is thus expressed in symbols:

Sulphurous oxide	SO_2
Sulphurous acid	$SO_3H_2 = SO_2.OH_2$
Sulphuric oxide	SO_3
Sulphuric acid	$SO_4H_2 = SO_3.OH_2$

† Sulphuric acid . . . . . SO_4H_2
Thiosulphuric acid . . . . . $S_2O_3H_2$.

‡ From πολὺς, many, and θεῖον, sulphur.

§ In symbols:

Dithionic acid	$S_2O_6H_2$
Trithionic acid	$S_3O_6H_2$
Tetrathionic acid	$S_4O_6H_2$
Pentathionic acid	$S_5O_6H_2$

‖ $2(SO_3.OH_2)$ + Cu = $SO_3.CuO$ + $2OH_2$ + SO_2
Sulphuric acid. Copper. Copper sulphate. Water. Sulphurous oxide.

for any length of time without change. When sulphurous oxide and aqueous vapor are passed into a vessel cooled to below —8·3° or —6° (17° or 21° F.), a crystalline body forms, which contains about 24·2 sulphurous oxide to 75·8 of water.

One volume of sulphurous oxide gas contains one volume of oxygen and half a volume of sulphur vapor, condensed into one volume.

Gases which, like the present, are freely soluble in water, must be collected by displacement, or by the use of the mercurial pneumatic trough. The manipulation with the latter is exactly the same in principle as with the ordinary water-trough, but rather more troublesome, from the great density of the mercury, and its opacity. The whole apparatus is on a much smaller scale. The trough is best constructed of hard, sound wood. and so contrived as to economize as much as possible the expensive liquid it is to contain.

Sulphurous acid has bleaching properties; it is used in the arts for bleaching woollen goods and straw-plait. A piece of blue litmus paper plunged into the moist gas is first reddened and then slowly bleached.

The salts of sulphurous acid are not of much importance: those of the alkalies are soluble and crystallizable; they are easily formed by direct combination. The sulphites of barium, strontium, and calcium are insoluble in water, but soluble in hydrochloric acid. The stronger acids decompose them; nitric acid converts them into sulphates.

Sulphurous oxide unites, under peculiar circumstances, with chlorine, and also with iodine, forming compounds, which have been called chloro- and iodo-sulphuric acids. They are decomposed by water. It also combines with dry ammoniacal gas, giving rise to a remarkable compound; and with nitric oxide also, in presence of an alkali.

Sulphur Trioxide or Sulphuric Oxide (also called *Anhydrous Sulphuric acid*, or *Sulphuric anhydride*). — This compound may be formed directly by passing a dry mixture of sulphurous oxide and oxygen gases over heated spongy platinum; or it may be obtained by distilling the most concentrated sulphuric acid with phosphoric oxide, which then abstracts the water and sets the sulphuric oxide free. It is usually prepared, however, from the fuming oil of vitriol of Nordhausen, which may be regarded as a solution of sulphuric oxide in sulphuric acid. On gently heating this liquid in a retort connected with a receiver cooled by a freezing mixture, the sulphuric oxide distils over in great abundance, and condenses into beautiful white silky crystals, resembling those of asbestos. When thrown into water, it hisses like a red-hot iron, from the violence with which combination occurs: the product is sulphuric acid. When exposed to the air, even for a few moments, it liquefies by absorption of moisture. It unites with ammoniacal gas, forming a salt called ammonium sulphamate, the nature of which will be explained further on.

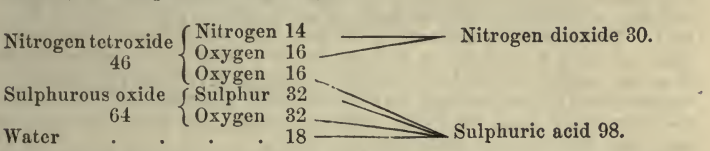
Sulphuric Acid. — This acid has been known since the fifteenth century. There are two distinct processes by which it is at present prepared — namely, by the distillation of ferrous sulphate (copperas or green vitriol), and by the oxidation of sulphurous acid with nitrous and hyponitric acids.

The first process is still carried on in some parts of Germany, especially in the neighborhood of Nordhausen in Prussia, and in Bohemia. The ferrous sulphate, derived from the oxidation of iron pyrites, is deprived by heat of the greater part of its water of crystallization, and subjected to a high red heat in earthen retorts, to which receivers are fitted as soon as the acid begins to distil over. A part gets decomposed by the very high temperature; the remainder is driven off in vapor, which is condensed by the cold vessel, containing a very small quantity of water or common sulphuric acid. The product is a brown oily liquid, of about 1·9 specific gravity, fum-

ing in the air, and very corrosive. It is chiefly made for the purpose of dissolving indigo.

The second method, which is, perhaps, with the single exception mentioned, always followed as the more economical, depends upon the fact that, when sulphurous oxide, nitrogen tetroxide, and water are present together in certain proportions, the sulphurous oxide becomes oxidized at the expense of the nitrogen tetroxide, which by the loss of one-half of its oxygen, sinks to the condition of nitrogen dioxide. The operation is thus conducted: A large and very long chamber is built of sheet-lead supported by timber-framing: on the outside, at one extremity, a small furnace or oven is constructed, having a wide tube leading into the chamber. In this, sulphur is kept burning, the flame of which heats a crucible containing a mixture of nitre and oil of vitriol. A shallow stratum of water occupies the floor of the chamber, and a jet of steam is also introduced. Lastly, an exit is provided at the remote end of the chamber for the spent and useless gases. The effect of these arrangements is to cause a constant supply of sulphurous oxide, atmospheric air, nitric acid vapor, and water in the state of steam, to be thrown into the chamber, there to mix and react upon each other. The nitric acid immediately gives up a part of its oxygen to the sulphurous oxide, and is itself reduced to nitrogen tetroxide; it does not remain in this state, however, but suffers further deoxidation until it becomes reduced to nitrogen dioxide. That substance, in contact with free oxygen, absorbs a portion of the latter, and once more becomes tetroxide, which is again destined to undergo deoxidation by a fresh quantity of sulphurous oxide. A very small portion of nitrogen tetroxide, mixed with atmospheric air and sulphurous oxide, may thus in time convert an indefinite amount of the latter into sulphuric acid, by acting as a kind of carrier between the oxygen of the air and the sulphurous oxide. The presence of water is essential to this reaction.

We may thus represent the change: *



Such is the simplest view that can be taken of the production of sulphuric acid in the leaden chamber; but it is too much to affirm that it is strictly true; the reaction may be more complex. When a little water is put at the bottom of a large glass globe, so as to maintain a certain degree of humidity in the air within, and sulphurous oxide and nitrogen tetroxide are introduced by separate tubes, symptoms of chemical action become immediately evident, and after a little time a white crystalline matter is observed to condense on the sides of the vessel. This substance appears to be a compound of sulphuric acid, nitrous acid, and a little water.† When thrown into water, it is resolved into sulphuric acid, nitrogen

* NO_2 (Nitrogen tetroxide.) + SO_2 (Sulphurous oxide.) + OH_2 (Water.) = NO (Nitrogen dioxide.) + SO_4H_2 (Sulphuric acid.)

† Gaultier de Claubry assigned to this curious substance the composition expressed by the formula $2(N_2O_3.2OH_2).5SO_3$, and this view has generally been received by recent chemical writers. De la Provostaye has since shown that a compound possessing all the essential properties of the body in question may be formed by bringing together, in a sealed glass tube, liquid sulphurous oxide and liquid nitrogen tetroxide, both free from water. The white crystalline solid soon begins to form, and at the expiration of twenty-six hours the reaction appears complete. The new product is accompanied by an exceedingly volatile greenish liquid

dioxide, and nitric acid. This curious body is certainly very often produced in large quantity in the leaden chambers; but that its production is indispensable to the success of the process, and constant when the operation goes on well, and the nitrogen tetroxide is not in excess, may perhaps admit of doubt.

The water at the bottom of the chamber thus becomes loaded with sulphuric acid: when a certain degree of strength has been reached, the acid is drawn off and concentrated by evaporation, first in leaden pans, and afterwards in stills of platinum, until it attains a density (when cold) of 1·84, or thereabouts; it is then transferred to carboys, or large glass bottles fitted in baskets, for sale. In Great Britain this manufacture is one of great national importance, and is carried on to a vast extent. Sulphuric acid is now more frequently made by burning iron pyrites, or poor copper ore, or zinc-blende, as a substitute for Sicilian sulphur: it very frequently contains arsenic, from which it may be freed, however, by heating it with a small quantity of sodium chloride, or by passing through the heated acid a current of hydrochloric acid gas, whereby the arsenic is volatilized as trichloride.

The most concentrated sulphuric acid, or *oil of vitriol*, as it is often called, is a definite combination of 40 parts sulphuric oxide, and 9 parts water.* It is a colorless oily liquid, having a specific gravity of about 1·85, of intensely acid taste and reaction. Organic matter is rapidly charred and destroyed by this substance. At the temperature of —26° (—15° F.) it freezes; at 327° (620° F.) it boils, and may be distilled without decomposition. Oil of vitriol has a most energetic attraction for water; it withdraws aqueous vapor from the air, and when it is diluted with water, great heat is evolved, so that the mixture always requires to be made with caution. Oil of vitriol is not the only hydrate of sulphuric oxide; three others are known to exist. When the fuming oil of vitriol of Nordhausen is exposed to a low temperature, a white crystalline substance separates, which is a hydrate containing half as much water as the common liquid acid. Then, again, a mixture of 98 parts of strong liquid acid and 18 parts of water † congeals or crystallizes at a temperature above 0°, and remains solid even at 7·2° (45° F.). Lastly, when a very dilute acid is concentrated by evaporation in a vacuum over a surface of oil of vitriol, the evaporation stops when the sulphuric oxide and water bear to each other the proportion of 80 to 54.‡

When the vapor of sulphuric acid is passed over red-hot platinum, it is decomposed into oxygen and sulphurous acid. St. Claire Deville and Debray have recommended this process for the preparation of oxygen on the large scale, the sulphurous acid being easily separated by its solubility in water or alkaline solutions.

Sulphuric acid acts readily on metallic oxides; converting them into sulphates. It also decomposes carbonates with the greatest ease, expelling carbon dioxide with effervescence. With the aid of heat it likewise decomposes all other salts containing acids more volatile than itself. The sulphates are a very important class of salts, many of them being extensively used in the arts. Most sulphates are soluble in water, but they are all insoluble in alcohol. The barium, calcium, strontium, and lead salts

having the characters of nitrous acid. The white substance, on analysis, was found to contain the elements of two molecules of sulphuric oxide and one of nitrous oxide, or $N_2O_3.2SO_3$. M. de la Provostaye very ingeniously explains the anomalies in the different analyses of the leaden chamber product, by showing that the pure substance forms crystallizable combinations with different proportions of sulphuric acid. (Ann. Chim. Phys. lxxiii. 362.) See also Weber (Jahresbericht für Chemie, 1863, p. 738; 1865, p. 93; Bull. Soc. Chim. de Paris, 1867, i. 15.)

* $SO_3.OH_2 = SO_4H_2$.

† $SO_3.2OH_2 = SO_4H_2.OH_2$.

‡ $SO_3\ 3OH_2 = SO_4H_2.2OH_2$.

are insoluble, or very slightly soluble, in water; and are formed by precipitating a soluble salt of either of those metals with sulphuric acid, or a soluble metallic sulphate. Barium sulphate is quite insoluble in water; consequently sulphuric acid, or its soluble salts, may be detected with the greatest ease by solution of barium nitrate or chloride; a white precipitate is thereby produced which does not dissolve in nitric acid.

Hyposulphurous, or Thiosulphuric Acid. — By digesting sulphur with a solution of potassium or sodium sulphite, a portion of that substance is dissolved, and the liquid, by slow evaporation, furnishes crystals of hyposulphite.* The acid itself is scarcely known, for it cannot be isolated: when hydrochloric acid is added to a solution of a hyposulphite, the acid of the latter is almost instantly resolved into sulphur, which precipitates, and sulphurous acid, easily recognized by its odor. In very dilute solution, however, it appears to remain undecomposed for some time. The most remarkable feature of the alkaline hyposulphites is their property of dissolving certain insoluble salts of silver, as the chloride — a property which has lately conferred upon them a considerable share of importance in relation to the art of photography. They are also much used as *antichlores* for removing the last traces of chlorine from bleached goods.

Dithionic, or Hyposulphuric Acid. — This acid is prepared by suspending finely divided manganese dioxide in water artificially cooled, and then transmitting a stream of sulphurous acid gas; the dioxide becomes monoxide, half its oxygen converting the sulphurous into dithionic acid.† The manganese dithionate thus prepared is decomposed by a solution of pure barium hydrate, and the barium salt, in turn, by enough sulphuric acid to precipitate the base. The solution of dithionic acid may be concentrated by evaporation in a vacuum, until it acquires a density of 1·347; pushed further, it decomposes into sulphuric and sulphurous acids. It has no odor, is very sour, and forms soluble salts with baryta, lime, and lead oxide.

Trithionic Acid. — A substance accidentally formed by Langlois,‡ in the preparation of potassium hyposulphite, by gently heating with sulphur a solution of potassium carbonate saturated with sulphurous acid. It is also produced by the action of sulphurous oxide on potassium hyposulphite.§ Its salts bear a great resemblance to those of hyposulphurous acid, but differ completely in composition, while the acid itself is not quite so prone to change. It is obtained by decomposing the potassium salt with hydrofluosilicic acid: it may be concentrated under the receiver of the air-pump, but is gradually decomposed into sulphur, sulphurous and sulphuric acids.

Tetrathionic Acid. — This acid was discovered by Fordos and Gélis.‖ When iodine is added to a solution of barium hyposulphite, a large quantity of that substance is dissolved, and a clear colorless solution obtained,

* SO_3K_2 (Potassium sulphite.) + S (Sulphur.) = $S_2O_3K_2$ (Potassium hyposulphite.)

† MnO_2 (Manganese dioxide.) + $2SO_3H_2$ (Sulphurous acid.) = S_2O_6Mn (Manganese dithionate.) + $2OH_2$ (Water.)

‡ Ann. Chim. Phys. [2], lxxiv. 250.

§ $2S_2O_3K_2$ (Potassium hyposulphite.) + $3SO_2$ (Sulphurous oxide.) = $2S_3O_6K_2$ (Potassium trithionate.) + S

‖ Ann. Ch. Pharm. xliv. 247.

which, besides barium iodide, contains barium tetrathionate.* By suitable means, the acid can be eliminated, and obtained in a state of solution. It very closely resembles dithionic acid. The same acid is produced by the action of sulphurous acid on chlorine disulphide.

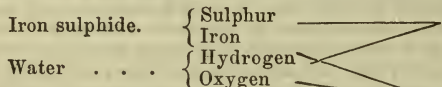
Pentathionic Acid. — Another acid of sulphur was discovered by Wackenroder,† who formed it by the action of hydrogen sulphide on sulphurous acid.‡ It is colorless and inodorous, of acid and bitter taste, and capable of being concentrated to a considerable extent by cautious evaporation.

Under the influence of heat, it is decomposed into sulphur, sulphurous and sulphuric acids, and hydrogen sulphide. The salts of pentathionic acid are nearly all soluble. The barium salt crystallizes from alcohol in square prisms. The acid is also formed when lead dithionate is decomposed by hydrogen sulphide, and when chlorine monosulphide is heated with sulphurous acid.

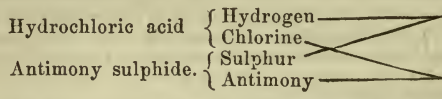
Sulphur with Hydrogen.

Hydrogen Monosulphide; Sulphydric Acid; Hydrosulphuric Acid; Sulphuretted Hydrogen.—There are two methods by which this important compound can be readily prepared, namely, by the action of dilute sulphuric acid upon iron monosulphide, and by the decomposition of antimony trisulphide with hydrochloric acid. The first method yields it most easily, the second in the purest state.

Iron monosulphide is put into the apparatus for hydrogen, already several times mentioned, together with water, and oil of vitriol is added by the funnel, until a copious disengagement of gas takes place. This is to be collected over tepid water. The reaction is thus explained: —



By the other plan, finely powdered antimony trisulphide is put into a flask to which a cork and bent tube can be adapted, and strong liquid hydrochloric acid poured upon it. On the application of heat, a double interchange occurs between the bodies present, hydrogen sulphide and antimony trichloride being formed. The action lasts only while the heat is maintained.



Hydrogen sulphide is a colorless gas, having the odor of putrid eggs; it is most offensive when in small quantity, when a mere trace is present in the air. It is not irritating, but, on the contrary, powerfully narcotic.

* $2S_2O_3Ba + I_2 = BaI_2 + S_4O_6Ba$
Barium hyposulphite. Iodine. Barium iodide. Barium tetrathionate.

† Ann. Ch. Pharm. lx. 189.

‡ $5SO_3H_2 + 5SH_2 = S_5O_6H_2 = 9OH_2 + S_5$
Sulphurous acid. Hydrogen sulphide. Pentathionic acid. Water. Sulphur.

§ $FeS + SO_4H_2 = SH_2 = SO_4Fe$
Ferrous sulphide. Hydrogen sulphate. Hydrogen sulphide. Ferrous sulphate.

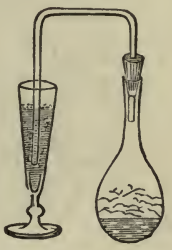
‖ $Sb_2S_3 + 6HCl = 3SH_2 + 2SbCl_3$
Antimonious sulphide. Hydrogen chloride. Hydrogen sulphide. Antimonious chloride.

When set on fire, it burns with a blue flame, producing sulphurous acid when the supply of air is abundant; and depositing sulphur when the oxygen is deficient. Mixed with chlorine, it is instantly decomposed, with separation of the whole of the sulphur.

This gas has a specific gravity of 1·171 referred to air, or 17 referred to hydrogen as unity; a litre weighs 1·51991 grams.

A pressure of 17 atmospheres at 10° (50° F.) reduces it to the liquid form. Cold water dissolves its own volume of hydrogen sulphide, and the solution is often directed to be kept as a test; it is so prone to decomposition, however, by the oxygen of the air, that it quickly spoils. A much better plan is to keep a little apparatus for generating the gas always at hand, and ready for use at a moment's notice. A small bottle or flask, to which a bit of bent tube is fitted by a cork, is supplied with a little iron sulphide and water; when required for use, a few drops of oil of vitriol are added, and the gas is at once evolved. The experiment completed, the liquid is poured from the bottle, replaced by a little clean water, and the apparatus is again ready for use.

Fig. 138.



Potassium heated in hydrogen sulphide burns with great energy, becoming converted into sulphide, while pure hydrogen remains, equal in volume to the original gas. Taking this act into account, and comparing the density of the gas with those of hydrogen and sulphur vapor, it appears that every volume of hydrogen sulphide contains one volume of hydrogen and half of a volume of sulphur-vapor, the whole condensed into one volume, a constitution precisely analogous to that of water-vapor. This corresponds very nearly with its composition by weight, determined by other means — namely, 16 parts sulphur and 1 part hydrogen.

When a mixture of 100 measures of hydrogen sulphide and 150 measures of pure oxygen is exploded by the electric spark, complete combustion ensues, and 100 measures of sulphurous oxide gas result.

Hydrogen sulphide is a frequent product of the putrefaction of organic matter, both animal and vegetable; it occurs also in certain mineral springs, as at Harrogate, and elsewhere. When accidentally present in the atmosphere of an apartment, it may be instantaneously destroyed by a small quantity of chlorine gas.

There are few reagents of greater value to the practical chemist than this substance: when brought in contact with many metallic solutions, it gives rise to precipitates, which are often exceedingly characteristic in appearance, and it frequently affords the means of separating metals from each other with the greatest precision and certainty. The precipitates spoken of are insoluble sulphides, formed by the mutual decomposition of the metallic oxides or chlorides and hydrogen sulphide, water or hydrochloric acid being produced at the same time. All the metals are in fact precipitated, whose sulphides are insoluble in water and in dilute acids.

Arsenic and cadmium solutions thus treated give bright yellow precipitates, the former soluble, the latter insoluble, in ammonium sulphide; tin salts give a brown or a yellow precipitate, according as the metal is in the form of a stannous or a stannic salt; both soluble in ammonium sulphide. Antimony solutions give an orange-red precipitate, soluble in ammonium sulphide. Copper, lead, bismuth, mercury, and silver salts give dark-brown or black precipitates, insoluble in ammonium sulphide; gold and platinum salts, black precipitates, soluble in ammonium sulphide.

Hydrogen sulphide possesses the properties of an acid; its solution in water reddens litmus-paper.

The best test for the presence of this compound is paper wetted with solution of lead acetate. This salt is blackened by the smallest trace of the gas.

Hydrogen disulphide. — This substance corresponds in constitution and instability to the hydrogen dioxide; it is prepared by the following means:

Equal weights of slaked lime and flowers of sulphur are boiled with 5 or 6 parts of water for half an hour, when a deep orange-colored solution is produced, containing, among other things, calcium disulphide. This is filtered, and slowly added to an excess of dilute sulphuric acid, with constant agitation. A white precipitate of separated sulphur and calcium sulphate makes its appearance, together with a quantity of yellow oily-looking matter, which collects at the bottom of the vessel: this is hydrogen disulphide.*

If the experiment be conducted by pouring the *acid* into the solution of the sulphide, then nothing but finely divided precipitated sulphur is obtained.

The disulphide is a yellow, viscid, insoluble liquid, exhaling the odor of sulphuretted hydrogen; its specific gravity is 1·769. It is slowly decomposed even in the cold into sulphur and hydrogen monosulphide, and instantly by a higher temperature, or by contact with many metallic oxides.

Carbon and Sulphur.

Carbon Disulphide or Bisulphide.† — A white porcelain tube is filled with pieces of charcoal which have been recently heated to redness in a covered crucible, and fixed across a furnace in a slightly inclined position. Into the lower extremity a tolerably wide tube is secured by the aid of a cork: this tube bends downward, and passes nearly to the bottom of a bottle filled with fragments of ice and a little water. The porcelain tube being heated to a bright redness, fragments of sulphur are thrown into the open end, which is immediately afterwards stopped by a cork. The sulphur melts, and becomes converted into vapor, which at that high temperature combines with the carbon, forming an exceedingly volatile compound, which is condensed by the ice and collects at the bottom of the vessel. This is collected and redistilled at a very gentle heat in a retort connected with a good condenser.

For preparation on the large scale, a tubulated earthen retort is filled with charcoal, and the sulphur is dropped in through a porcelain tube passing through the tubulus and reaching nearly to the bottom; or the charcoal is contained in a large iron cylinder, and the sulphur introduced through a pipe fitted into the lower part.

* The reaction which ensues when calcium hydrate, sulphur, and water are boiled together is rather complex, disulphide or pentasulphide of calcium being formed, together with calcium hyposulphite, arising from the transfer of the oxygen of the decomposed lime to another portion of sulphur.

$3CaO$	$+$	S_6	$=$	$2CaS_2$	$+$	S_2O_3Ca
Lime.		Sulphur.		Calcium disulphide.		Calcium hyposulphite.

The calcium disulphide, decomposed by an acid under favorable circumstances, yields a calcium salt and hydrogen disulphide.

CaS_2	$+$	SO_4H_2	$=$	SH_2	$+$	SO_4Ca
Calcium disulphide.		Sulphuric acid.		Hydrogen disulphide.		Calcium sulphate.

When the acid is poured into the sulphide, sulphuretted hydrogen, water, and calcium sulphate are produced, while the excess of sulphur is thrown down as a fine white powder, the "precipitated sulphur" of the Pharmacopœia. When the object is to prepare the latter substance, hydrochloric acid must be used in place of sulphuric acid.

† CS_2.

Carbon disulphide is a transparent, colorless liquid of great refractive and dispersive power. Its density is 1·272, that of its vapor is 2·67. It boils at 43° (110° F.), and emits vapor of considerable elasticity at common temperatures. This substance has a very repulsive odor. When set on fire in the air, it burns with a blue flame, forming carbon dioxide and sulphur dioxide gases; and when its vapor is mixed with oxygen, it becomes explosive. Carbon disulphide, when heated with water in a sealed tube to about 153° (307° F.), is converted into carbon dioxide and hydrogen sulphide. In contact with nascent hydrogen (when heated with zinc and dilute sulphuric acid), it is converted into a white crystalline substance containing carbon, hydrogen, and sulphur,* crystallizing in square prisms, insoluble in water, alcohol, and ether, but soluble in carbon disulphide, subliming at 150° (302° F.), and decomposing at 200°. Carbon disulphide freely dissolves sulphur, and by spontaneous evaporation deposits the latter in beautiful crystals; it also dissolves phosphorus, iodine, camphor, and caoutchouc, and mixes easily with oils. It is extensively used in the vulcanization of caoutchouc, and in the manufacture of gutta-percha, also for extracting bitumen from mineral substances, and oil from seeds.

Carbon disulphide unites with metallic sulphides, forming salts called *sulphocarbonates*, which have the composition of carbonates with the oxygen replaced by sulphur. By treating the ammonium salt with dilute sulphuric or hydrochloric acid, an oily acid liquid is precipitated, consisting of hydrogen sulphocarbonate, or sulphocarbonic acid.†

Compounds of Sulphur with Chlorine.

When dry chlorine is passed over the surface of sulphur kept melted in a small glass retort connected with a good condensing arrangement, a deep orange-yellow mobile liquid distils over, having a peculiar and disagreeable odor, and boiling at 136° (276° F.). As this substance dissolves both sulphur and chlorine, it is not easy to obtain it in a pure and definite state. It contains 32 parts sulphur and 35·5 chlorine, and is called *sulphur monochloride* (or *subchloride*), also *chlorine bisulphide.* ‡

It is instantly decomposed by water, hydrochloric and hyposulphurous acids being formed, and sulphur separated. The hyposulphurous acid in its turn decomposes into sulphur and sulphurous acid.§ By exposing the above compound for a considerable time to the action of chlorine, and then distilling it in a stream of the gas, a deep-red liquid is obtained, at a certain stage of the distillation, heavier than water, boiling at 164°, and containing twice as much chlorine as the monochloride, hence called *sulphur dichloride* or *chlorine monosulphide.*‖ It appears, however, to be not a definite compound of sulphur and chlorine, but a mixture of the preceding with the following compound.

A compound called *sulphur tetrachloride,*¶ containing 32 parts of sulphur to 142 parts of chlorine, appears to exist in combination with certain metallic chlorides, but is not known in the separate state. According to Carius,** the red-brown liquid, obtained as above mentioned by saturating chlorine disulphide with chlorine, is a mixture of the monochloride and

* CSH_2.

† Calcium carbonate . . . CO_3Ca = $CO_2.CaO$
Calcium sulpho-carbonate . CS_3Ca = $CS_2.CaS$
Hydrogen sulpho-carbonate CS_3H_2 = $CS_2.H_2S$

‡ SCl or S_2Cl_2.

§ $2S_2Cl_2 + 3H_2O = 4HCl + S_2 + S_2O_3H_2$ (or $SO_2H_2 + S$)
Sulphur monochloride. Water. Hydrochloric acid. Sulphur. Hyposulphurous acid. Sulphurous acid. Sulphur.

‖ SCl_2 or $S_2Cl_2 + SCl_4$.

¶ SCl_4.

** Ann. Ch. Pharm. cvi. 291; cx. 209; see also Watts's Dictionary of Chemistry, v. 533.

tetrachloride in various proportions, according to the temperature at which the saturation is effected.

Carbon Oxychloride.* — This compound, also called *phosgene gas*, has been already mentioned. It is produced by the direct combination of chlorine and carbon monoxide under the influence of sunshine; but is more easily prepared by passing carbon monoxide into boiling antimony pentachlorides. It must be received over mercury, as water decomposes it.

Carbon Sulphochloride.† — This compound, the sulphur-analogue of the preceding, is produced, together with chlorine monosulphide, by the action of dry chlorine on carbon disulphide,‡ or by passing a mixture of hydrogen sulphide and vapor of carbon tetrachloride through a red-hot tube.⁂ It is a yellow liquid having a very irritating odor, not acted upon by water or acids, but decomposed by potash, yielding potassium sulphide, potassium carbonate, and carbon tetrachloride. ‖

Sulphur and Bromine. — Bromine dissolves sulphur, forming a brown-red liquid probably containing a sulphur bromide analogous to sulphur monochloride; but it has not been obtained pure.

Sulphur and Iodine. — These elements combine when heated together, even under water. The resulting compound, containing 32 parts of sulphur and 127 parts of iodine,¶ is a blackish-gray radio-crystalline mass, resembling native antimony sulphide. It decomposes at higher temperatures, gives off iodine on exposure to the air, and is insoluble in water. By heating 254 parts of iodine with 32 parts of sulphur,** a compound is obtained which smells like iodine, and is said to be a powerful remedy in skin-diseases. A cinnabar-red sulphur iodide is obtained, according to Grosourdi, by precipitating iodine trichloride with hydrogen sulphide.

SELENIUM.

This is a very rare substance, much resembling sulphur in its chemical relations, and found in association with that element in some few localities, or replacing it in certain metallic combinations, as in the lead selenide of Clausthal in the Hartz.

Selenium is a reddish-brown solid body, somewhat translucent, and having an imperfect metallic lustre. Its specific gravity, when rapidly cooled after fusion, is 4·3. At 100°, or a little above, it melts, and boils. It is insoluble in water, and exhales, when heated in the air, a peculiar and disagreeable odor, which has been compared to that of decaying horse-radish: it is insoluble in alcohol, but dissolves slightly in carbon bisulphide, from which solution it crystallizes.

Two oxides of selenium are known. The one containing the smallest proportion of oxygen is formed by the imperfect combustion of selenium in air or oxygen gas. It is a colorless gas which is the source of the peculiar horse-radish odor above mentioned. Its composition is not known.

The higher oxide, called *selenious oxide*, is produced by burning selenium

* $COCl_2$. † $CSCl_2$.
‡ $CS_2 + Cl_4 = CSCl_2 + SCl_2$.
⁂ $CCl_4 + SH_2 = 2HCl + CSCl_2$.
‖ $2CSCl_2 + 3K_2O = 2K_2S + CO_3K_2 + CCl_4$.
¶ S_2I_2. ** SI_2.

in a stream of oxygen gas; it contains 79·5 parts, by weight, of selenium, and 32 of oxygen. It is a white solid substance which absorbs water rapidly, forming a hydrate, viz.:

	Selenium.	Oxygen.	Hydrogen.	Selenious oxide.	Water.
Selenious acid, or Hydrogen selenite	79·4	+ 48	+ 2	or 111·4	+ 18

This acid, analogous in composition and properties to sulphurous acid, is likewise produced by dissolving selenium in nitric or nitro-muriatic acid. It is deposited from its hot aqueous solution by slow cooling in prismatic crystals like those of saltpetre; but when the solution is evaporated to dryness, the selenious acid is resolved into water and selenious oxide, which sublimes at a higher temperature.

Selenious acid is a very powerful acid, approximating to sulphuric acid in the energy of its reactions. It reddens litmus, decomposes carbonates with effervescence, and decomposes nitrates and chlorides with aid of heat. Its solution precipitates lead and silver salts, and is decomposed by hydrogen sulphide, yielding a precipitate of selenium sulphide.*

The metallic selenites resemble the sulphites. When heated with sodium carbonate in the inner blowpipe flames, they emit the characteristic odor of selenium. They are not decomposed by boiling with hydrochloric acid.

Selenic Acid is a more highly oxidized acid of selenium, analogous to sulphuric acid, and containing 79·4 parts, by weight, of selenium, 64 of oxygen, and 2 of hydrogen.† The corresponding anhydrous oxide is not known. Selenic acid is prepared by fusing potassium or sodium nitrate with selenium, precipitating the selenate so produced with a lead salt, and then decomposing the compound with hydrogen sulphide. The acid strongly resembles oil of vitriol; but, when very much concentrated, decomposes, by the application of heat, into selenious acid and oxygen. The selenates bear the closest analogy to the sulphates in almost every particular. They are decomposed by boiling with hydrochloric acid, chlorine being evolved and a salt of selenious acid being produced.

Hydrogen Selenide; Selenhydric Acid; Selenetted Hydrogen. — This substance is produced by the action of dilute sulphuric acid upon potassium or iron selenide. It very much resembles sulphuretted hydrogen, being a colorless gas, freely soluble in water, and decomposing metallic solutions like that substance: insoluble selenides are thus produced. This gas is said to act very powerfully upon the lining membrane of the nose, exciting catarrhal symptoms, and destroying the sense of smell. It contains 79·4 parts selenium and 2 parts hydrogen.‡

TELLURIUM.

This element possesses many of the characters of a metal, but it bears so close a resemblance to selenium, both in its physical properties and its chemical relations, that it is most appropriately placed in the same group with that body. Tellurium is found in a few scarce minerals in association

* SeO_2H_2 + $2SH_2$ = $3OH_2$ + SeS_2.
Selenious acid. Hydrogen sulphide. Water.

† Selenic acid, SeO_4H_2.

‡ SeH_2.

with gold, silver, lead, and bismuth, apparently replacing sulphur, and is most easily extracted from the bismuth sulpho-telluride of Chemnitz in Hungary. The finely powdered ore is mixed with an equal weight of dry sodium carbonate, the mixture made into a paste with oil, and heated to whiteness in a closely covered crucible. Sodium telluride and sulphide are thereby produced, and metallic bismuth is set free. The fused mass is dissolved in water, and the solution freely exposed to the air, when the sodium and sulphur oxidize to sodium hydrate and hyposulphite, while the tellurium separates in the metallic state.

Tellurium has the color and lustre of silver; by fusion and slow cooling it may be made to exhibit the form of rhombohedral crystals similar to those of antimony and arsenic. It is brittle, and a comparatively bad conductor of heat and electricity: it has a density of 6·26, melts at a little below a red-heat, and volatilizes at a higher temperature. Tellurium burns when heated in the air, and is oxidized by nitric acid.

Tellurium forms two oxides, analogous in composition to the oxides of sulphur, and likewise forming acids by combination with water.

	Composition by weight.*				
	Tellurium.		Oxygen.		Hydrogen.
Tellurous oxide . . .	128	+	32		
——— acid . .	128	+	48	+	2
Telluric oxide . . .	128	+	48		
——— acid . . .	128	+	64	+	2

Tellurous Oxide may be prepared by heating the precipitated acid to low redness. It also separates in semi-crystalline grains from the aqueous solution of the acid when gently heated; more abundantly and in well defined octohedrons from the solution of tellurous acid in nitric acid. It is fusible and volatile, slightly soluble in water, but does not redden litmus. When fused with alkaline hydrates or carbonates, it forms tellurites.

Tellurous Acid is best obtained by decomposing tellurium tetrachloride with water. It may also be prepared by dissolving tellurium in nitric acid of spec. gr. 1·25, and pouring the solution, after a few minutes, into a mass of water. By either process it is obtained as a somewhat bulky precipitate, which, when dried over oil of vitriol, appears as a light, white, earthy mass, having a bitter metallic taste. It is slightly soluble in water, more easily soluble in alkalies and acids, the nitric acid solution alone being unstable. Sulphurous acid, zinc, phosphorus, and other reducing agents, precipitate metallic tellurium from the acidified solution of tellurous acid. Like selenious acid, it is decomposed by hydrogen sulphide and alkaline sulph-hydrates, with formation of a dark-brown tellurium sulphide, which dissolves readily in excess of alkaline sulph-hydrate, forming a sulphotellurite.

Tellurous acid is a hydrate in which the acid and basic tendencies are nearly balanced; in other words, the tellurium of the compound can replace the hydrogen of an acid to form tellurous salts, and the hydrogen of the compound can be replaced by the basylous metals, to form metallic tellurites.† The tellurites of potassium, sodium, barium, strontium, and cal-

* Tellurous oxide TeO_2
——— acid TeO_3H_2 = $TeO_2.OH_2$.
Telluric oxide TeO_3
——— acid TeO_4H_2 = $TeO_3.OH_2$.

† Tellurium Salts.
$Te(SO_4)_2$ Sulphate.
$Te(NO_3)_4$ Nitrate.
$Te(C_2O_4)_2$ Oxalate.
$TeCl_4$ Chloride.

Tellurites.
TeO_3H_2 Hydrogen tellurite.
TeO_3K_2 Potassium tellurite.
TeO_3KH Hydrogen and potassium tellurite.
$(TeO_3)_2KH_3$ Trihydropotassic tellurite.

cium, are formed by fusing tellurous oxide, or acid, with the carbonates of the several metals in the required proportions. These tellurites are all more or less soluble in water. The tellurites of the other metals, which are insoluble, are obtained by precipitation.

Telluric Oxide and Acid. — Equal parts of tellurous oxide and sodium carbonate are fused, and the product is dissolved in water; a little sodium hydrate is added, and a stream of chlorine passed through the solution. The liquid is next saturated with ammonia, and mixed with solution of barium chloride, by which a white insoluble precipitate of barium tellurate is thrown down. This is washed and digested with a quarter of its weight of sulphuric acid, and diluted with water. The filtered solution gives, on evaporation in the air, large crystals of telluric acid, containing water of crystallization.*

Crystallized telluric acid is freely, although slowly, soluble in water; it has a metallic taste, and reddens litmus-paper. The crystals give off their water of crystallization at 100°, and the remaining acid, when strongly heated, gives off more water and yields the anhydrous oxide, which is then insoluble in water, and even in a boiling alkaline liquid. At the temperature of ignition, telluric oxide loses oxygen, and passes into tellurous oxide.

The tellurates of the alkali-metals† are soluble in water, and are prepared by dissolving the required quantities of telluric acid and an alkaline carbonate in hot water. The other tellurates are insoluble, and are obtained by precipitation.

Tellurium Sulphides.‡ — Tellurium forms two sulphides, analogous in composition to the oxides; they are formed by the action of hydrogen sulphide on solutions of tellurous acid and telluric acid respectively. They are brown or black substances, which unite with metallic sulphides, forming salts called sulphotellurites and sulphotellurates.

Hydrogen Telluride. — *Tellurhydric acid*, *Hydrotelluric acid*, or *Telluretted Hydrogen.* § — This compound is a gas, resembling sulphuretted and selenietted hydrogen. It is prepared by the action of hydrochloric acid on zinc telluride. It dissolves in water, forming a colorless liquid, which precipitates most metals from their solutions, and deposits tellurium on exposure to the air.

Tellurium Chlorides. ‖ — Tellurium forms a dichloride and a tetrachloride, both volatile and decomposable by excess of water, the latter being completely resolved into tellurous and hydrochloric acids.¶ The tetrachloride unites with the chlorides of the alkali-metals, to form crystallizable double salts.

The *bromides* and *iodides of tellurium* correspond to the chlorides in properties and composition.

* Crystallized telluric acid, $TeO_4H_2.2OH_2$; acid dried at 100°, TeO_4H_2.

† Neutral potassium tellurate . . . . . TeO_4K_2
Acid . . . . . TeO_4KH
Quadracid . . . . . $TeO_4KH.TeO_4H_2$
Anhydrous quadritellurate . . . . . $TeO_4K_2.3TeO_4$.

‡ TeS_2 and TeS_2. § TeH_2. ‖ $TeCl_2$ and $TeCl_4$.

¶ $TeCl_4 + 3H_2O = 4HCl + TeO_3H_2$.

BORON.

This element, the basis of boric or boracic acid, is prepared by heating the double fluoride of boron and potassium with metallic potassium in a small iron vessel, and washing out the soluble salts with water. It is a dull, greenish-brown powder, which burns in the air when heated, producing boric oxide. Nitric acid, alkalies in the fused state, chlorine, and other agents, attack it readily.

By a process analogous to that adopted for the preparation of the diamond variety of silicium, Wöhler and Deville have procured also the corresponding modification of boron. It crystallizes in square octohedrons, generally of a brownish color, possessing very nearly the hardness and refractive power of diamond. It is infusible in the flame of the oxy-hydrogen blowpipe, but burns in oxygen at the same temperature at which the diamond is oxidized. Its specific gravity is 2·68.

By fusing boric oxide with aluminium, Wöhler and Deville likewise obtained, together with diamond boron, a small quantity of graphite-like substance which they at first regarded as a graphitoïdal modification of boron; but by more recent experiments, they have found that it is a compound of boron with aluminium. This compound is obtained in larger quantity by passing the vapor of boric chloride over fused aluminium. It crystallizes in thin opaque six-sided plates, having a pale copper-color, and perfect metallic lustre.

Boric Oxide and Acid.*—There is but one oxide of boron, namely, boric oxide, containing 11 parts of boron and 48 of oxygen. It unites with water and metallic oxides, forming boric acid and metallic borates.

Boric or Boracic Acid, or Hydrogen Borate, contains 11 parts boron, 48 oxygen, and 3 hydrogen, or 7 parts boric oxide, and 54 water. It is found in solution in the water of the hot volcanic lagoons of Tuscany, whence a large supply is at present derived. It is also easily made by decomposing with sulphuric acid a hot solution of borax, a salt brought from the East Indies, consisting of sodium borate.

Boric acid crystallizes in transparent colorless plates, soluble in about 25 parts of cold water, and in a much smaller quantity at the boiling heat; the acid has but little taste, and feebly affects vegetable colors. When heated, it loses water, and melts to a glassy transparent mass of anhydrous boric oxide, which dissolves many metallic oxides with great ease. The crystals dissolve in alcohol, and the solution burns with a green flame.

Glassy boric oxide, in a state of fusion requires for its dissipation in vapor a very intense and long-continued heat; the aqueous solution cannot, however, be evaporated without very appreciable loss by volatilization: hence it is probable that the acid is far more volatile than the anhydrous oxide.

By heating in a glass flask or retort, 1 part of vitrified boric oxide, 2 of fluor-spar, and 12 of oil of vitriol, a gaseous *boron fluoride*† may be obtained, and received in glass jars standing over mercury. It is a transparent gas, easily soluble in water, and very heavy; it forms a dense fume in the air, like the fluoride of silicium.

Boron Nitride.‡—This compound, containing 11 parts of boron and 14 of nitrogen, is produced by heating boric oxide with metallic cyanides, or

* Boric oxide, B_2O_3. Boric acid, B_2O_3, $3H_2O$, or BO_3H_3.
† BF_3. ‡ BN.

by heating to bright redness a mixture of sal-ammoniac and pure anhydrous borax.* It is a white amorphous powder, insoluble in water, infusible and non-volatile. When heated in a current of steam, it yields ammonia and boric oxide,† and likewise gives off a large quantity of ammonia when fused with potash.

Boron Chloride‡ was formerly believed to be a permanent gas: recent researches have proved that it is a liquid, boiling at 17°, decomposed by water, with production of boric and hydrochloric acids, and fuming strongly in the air. It may be most easily obtained by exposing to the action of dry chlorine at a very high temperature an intimate mixture of glassy boric oxide and charcoal. It resembles in constitution the lower chloride of phosphorus.

There is also a *Boron bromide* ‖ of similar constitution.

SILICIUM.

Silicium, sometimes called silicon, in union with oxygen constituting silica, or the earth of flints, is a very abundant substance, and one of great importance. It enters largely into the composition of many of the rocks and mineral masses of which the surface of the earth is composed. The following process yields silicium most readily. The double fluoride of silicium and potassium is heated in a glass tube with nearly its own weight of metallic potassium; violent reaction ensues, and silicium is set free. When cold, the contents of the tube are put into cold water, which removes the saline matter and any residual potassium, and leaves the silicium untouched. So prepared, silicium is a dark-brown powder, destitute of lustre. Heated in the air, it burns, and becomes superficially converted into silica. It is also acted upon by sulphur and by chlorine. When silicium is strongly heated in a covered crucible, its properties are greatly changed; it becomes darker in color, denser, and incombustible, refusing to burn even when heated by the flame of the oxy-hydrogen blowpipe.

According to recent researches by Wöhler and Deville, silicium, like carbon, is capable of existing in three different modifications. The modification above mentioned corresponds to the amorphous variety of carbon (lampblack). The researches just quoted have established the existence of modifications corresponding to the diamond, and to the graphite variety of carbon. The diamond modification of silicium is most readily obtained by introducing into a red-hot crucible a mixture of 3 parts of potassium silico-fluoride, 1 part of sodium in small fragments, and 1 part of granulated zinc, and heating to perfect fusion. On slowly cooling, there is formed a button of zinc, covered and interspersed with needle-shaped crystals consisting of octohedrons, joined in the direction of the axis. This crystallized silicium, which may be readily freed from zinc by treatment with acids, resembles crystallized hæmatite in color and appearance: it scratches glass, and fuses at a temperature approaching the melting-point

* $Na_2O.2B_2O_3$ (Anhydrous sodium borate.) + $2NH_4Cl$ (Ammonium chloride.) = $2BN$ (Boron nitride.) + B_2O_3 (Boric oxide.) + $2NaCl$ (Sodium chloride.) + $4OH_2$ (Water.)

† $2BN$ (Boron nitride.) + $3OH_2$ (Water.) = $2NH_3$ (Ammonia.) + B_2O_3 (Boric oxide.)

‡ BCl_3.

‖ BBr_3.

of cast iron. The graphite modification of silicium is prepared by fusing, in a Hessian crucible, 5 parts of soluble glass (potassium silicate), 10 parts of cryolite (sodium and aluminium fluoride), with 1 part of aluminium. On treating the resulting button of aluminium with hydrochloric acid, the silicium remains in the form of scaly crystals, resembling graphite, but of somewhat brighter color, scratching glass, like the previous modification. It is infusible. Its specific gravity is 2·49.

Fig. 139.

Silica, or Silicic Oxide. — This is the only known oxide; it contains 28 parts silicium and 32 parts oxygen.* Colorless transparent rock-crystal consists of silica very nearly in a state of purity; common quartz, agate, chalcedony, flint, and several other minerals, are also chiefly composed of this substance.

The experiment about to be described furnishes silica in a state of complete purity, and at the same time exhibits one of the most remarkable properties of silicium — namely, its attraction for fluorine. A mixture is made of equal parts fluor-spar and glass, both finely powdered and introduced into a glass flask, with a quantity of oil of vitriol. A tolerably wide bent tube, fitted to the flask by a cork, passes to the bottom of a glass jar, into which enough mercury is poured to cover the extremity of the tube. The jar is then half filled with water, and heat is applied to the flask.

The first effect is the disengagement of hydrofluoric acid: this substance, however, finding itself in contact with the silica of the powdered glass, undergoes decomposition, water and silicium fluoride being produced. The latter is a permanent gas, which escapes from the flask by the bent tube. By contact with a large quantity of water, it is in turn decomposed, yielding silica, which separates in a beautiful gelatinous condition, and an acid liquid, which is a double silicium and hydrogen fluoride, commonly called hydrofluosilicic or silicofluoric acid.† The silica may be collected on a cloth filter, well washed, dried, and heated to redness to expel water.

The acid liquid is kept as a test for barium and potassium, with which it forms nearly insoluble precipitates, the double fluoride of silicium and potassium being used, as was stated, in the preparation of silicium. Silicium fluoride, instead of being condensed into water, may be collected over mercury: it is a permanent gas, destitute of color, and very heavy. Admitted into the air, it condenses the moisture of the latter, giving rise to a thick white cloud. It is important in the experiment above described to keep the end of the delivery-tube from touching the water of the jar, otherwise it almost instantly becomes stopped: the mercury effects this object.

Pure silica may also be prepared by another method, which is very instructive, inasmuch as it is the basis of the proceeding adopted in the analysis of all siliceous minerals. Powdered rock-crystal or fine sand is mixed with about three times its weight of dry sodium carbonate, and the mixture fused in a platinum crucible. When cold, the glassy mass is boiled with water, by which it is softened and almost entirely dissolved. An excess of hydrochloric acid is then added to the filtered liquid, and the whole

* SiO_2.

† (1) Reaction of hydro-fluoric acid upon silica:

$$\underset{\text{Hydrofluoric acid.}}{4HF} + \underset{\text{Silica.}}{SiO_2} = \underset{\text{Water.}}{2OH_2} + \underset{\text{Silicium fluoride.}}{SiF_4}$$

(2) Decomposition of fluoride of silicium by water:

$$\underset{\text{Silicium fluoride.}}{SiF_4} + \underset{\text{Water.}}{OH_2} = \underset{\text{Silica.}}{SiO_2} + \underset{\text{Hydrofluosilicic acid.}}{2HF,SiF_4}$$

evaporated to complete dryness. By this treatment the gelatinous silica thrown down by the acid becomes completely insoluble, and remains behind when the dry saline mass is treated with acidulated water, by which the alkaline salts, alumina, ferric oxide, lime, and many other bodies which may happen to be present, are removed. The silica is washed, dried, and heated to redness.

The most prominent characters of silica are the following: it is a very fine, white, tasteless powder, having a density of about 2·66, fusible only by the oxy-hydrogen blowpipe. When once dried, silica is not sensibly soluble in water or dilute acids (with the exception of hydrofluoric acid). But on adding hydrochloric acid to a very dilute solution of potassium silicate, the liberated silica remains in solution. From this mixed solution of silica and potassium chloride, the latter may be separated by diffusion (comp. p. 149), whereby a moderately concentrated solution of silica in water is obtained. This solution has a distinctly acid reaction: it presents, however, but little stability. When kept for some time, it gelatinizes, the silica separating in the insoluble modification. The same effect is produced by the addition of a few drops of sulphuric or nitric acid, or of a solution of salt.

Silica is essentially an acid oxide, forming salts with basic metallic oxides, and decomposing all salts of volatile acids when heated with them. In strong alkaline liquids it is freely soluble. When heated with bases, especially those which are capable of undergoing fusion, it unites with them and forms salts, which are sometimes soluble in water, as in the case of the potassium and sodium silicates, when the proportion of base is considerable. Common glass is a mixture of several silicates, in which the reverse of this happens, the silica being in excess. Even glass, however, is slowly acted upon by water.

Finely divided silica is highly useful in the manufacture of porcelain.

Silicium Hydride, or Silicated Hydrogen, was discovered by Buff and Wöhler, who obtained this gas by passing an electric current through a solution of sodium chloride, the positive pole employed consisting of aluminium containing silicium. More recently Wöhler and Martius produced this gas by treating magnesium containing silicium with hydrochloric acid. Both methods yield silicium hydride mixed with free hydrogen. Friedel and Ladenburg, however, by a process which will be described further on, have obtained it pure, and shown that it consists of 28 parts by weight of silicium and 4 parts of hydrogen.* Silicium hydride is a colorless gas. In the impure state, as obtained by the two processes above given, it takes fire spontaneously on coming in contact with the air, and burns with a white flame evolving clouds of silica. Pure silicium hydride, however, does not ignite spontaneously under the ordinary atmospheric pressure; but on passing a bubble of air into the rarefied gas standing over mercury, it takes fire, and yields a deposit of amorphous silicium mixed with silica. On passing silicium hydride through a red-hot tube, it is decomposed, silicium being deposited.

Compounds of Silicium and Chlorine. — Silicium unites directly with chlorine, forming a tetrachloride.† This compound is obtained by mixing finely divided silica with charcoal powder and oil, strongly heating the mixture in a covered crucible, and then exposing the mass so obtained in a porcelain tube heated to full redness, to the action of perfectly dry chlorine gas. A good condensing arrangement, supplied with ice-cold water, must be connected with the porcelain tube. The product is a colorless and very volatile liquid, boiling at 50°, of pungent, suffocating odor. In contact

* SiH_4. † $SiCl_4$.

with water, it yields hydrochloric acid and gelatinous silica. This substance contains 28 parts silicium and 142 chlorine.

When hydrochloric acid gas is passed over crystallized silicium, heated to a temperature below redness, a very volatile inflammable liquid is obtained, which, when purified by distillation, has the composition of *silicium hydrotrichloride*,* containing 28 parts silicium, 1 hydrogen, and 106·5 chlorine. This compound is decomposed by water, forming a white oxygenated body, probably *silicium hydrotrioxide*,† which by prolonged contact with water is further decomposed, with evolution of hydrogen and formation of silica.

A mixture of silicium hydrotrichloride and bromine, heated to 100° in a closed vessel, becomes dark-colored, and is converted into the *bromotrichloride*. ‡

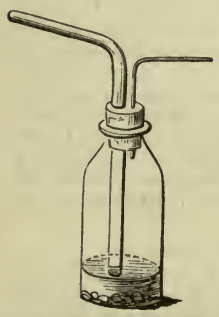
Silicium tetrabromide,§ obtained like the tetrachloride, resembles that compound, but is less volatile.

PHOSPHORUS.

Phosphorus in the state of phosphoric acid is contained in the ancient unstratified rocks, and in the lavas of modern origin. As these disintegrate and crumble down into fertile soil, the phosphates pass into the organism of plants, and ultimately into the bodies of the animals to which these latter serve for food. The earthy phosphates play a very important part in the structure of the animal frame, by communicating stiffness and inflexibility to the bony skeleton.

Phosphorus was discovered in 1669 by Brandt, of Hamburg, who prepared it from urine. The following is an outline of the process now adopted. Thoroughly calcined bones are reduced to powder, and mixed with two thirds of their weight of sulphuric acid diluted with a considerable quantity of water: this mixture, after standing some hours, is filtered, and the nearly insoluble calcium sulphate is washed. The liquid is then evaporated to a syrupy consistence, mixed with charcoal powder, and the desiccation completed in an iron vessel exposed to a high temperature. When quite dry, it is transferred to a stoneware retort, to which a wide, bent tube is luted, dipping a little way into the water contained in the receiver. A narrow tube serves to give issue to the gases, which are conveyed to a chimney. This manufacture is now conducted on a very large scale, the consumption of phosphorus, for the apparently trifling article of instantaneous-light matches, being something prodigious.

Fig. 140.



Phosphorus, when pure, very much resembles in appearance imperfectly bleached wax, and is soft and flexible at common temperatures. Its density is 1·77, and that of its vapor 4·35, air being unity, or 62 referred to hydrogen as unity. It melts at 44° (111° F.), and boils at 280° (536° F.). On slowly cooling melted phosphorus, well formed dodecahedrons are sometimes obtained. It is insoluble in water, and is usually kept immersed in

* $SiHCl_3$. † $Si_2H_2O_3$. ‡ $SiBrCl_3$. § $SiBr_4$.

that liquid, but dissolves in oils, in native naphtha, and especially in carbon bisulphide. When set on fire in the air, it burns with a bright flame, generating phosphoric oxide. Phosphorus is exceedingly inflammable; it sometimes takes fire by the heat of the hand, and demands great care in its management; a blow or hard rub will very often kindle it. A stick of phosphorus held in the air always appears to emit a whitish smoke, which in the dark is luminous. This effect is chiefly due to a slow combustion which the phosphorus undergoes by the oxygen of the air, and upon it depends one of the methods employed for the analysis of air, as already described. It is singular that the slow oxidation of phosphorus may be entirely prevented by the presence of a small quantity of olefiant gas, or the vapor of ether, or some essential oil; phosphorus may even be distilled in an atmosphere containing vapor of oil of turpentine in considerable quantity. Neither does the action go on in pure oxygen — at least, at the temperature of 15·5° (60° F.), which is very remarkable; but if the gas be rarefied, or diluted with nitrogen, hydrogen, or carbonic acid, oxidation is set up.

A very remarkable modification of this element is known by the name of *amorphous phosphorus.* It was discovered by Schrötter, and may be made by exposing common phosphorus for fifty hours to a temperature of from 240° to 250°, (464°–482 F°.), in an atmosphere which is unable to act chemically upon it. At this temperature it becomes red and opaque, and insoluble in carbon bisulphide, whereby it may be separated from ordinary phosphorus. It may be obtained in compact masses when common phosphorus is kept for eight days at a constant high temperature. It is a coherent, reddish-brown, infusible substance, of specific gravity between 2·089 and 2·106. It does not become luminous in the dark until its temperature is raised to about 200°, nor has it any tendency to combine with the oxygen of the air. When heated to 260° (500° F.), it is reconverted into ordinary phosphorus.

Compounds of Phosphorus and Oxygen.

When phosphorus is melted beneath the surface of hot water, and a stream of oxygen gas forced upon it from a bladder, combustion ensues, and the phosphorus is converted in great part into a brick-red powder, which was formerly believed to be a peculiar oxide of phosphorus; but Schrötter has shown that it is a mixture, consisting chiefly of amorphous phosphorus.

There are two definite oxides of phosphorus, in which the quantities of oxygen united with the same quantity of phosphorus are to one another as 3 to 5,* viz.:

	Composition by weight.	
	Phosphorus.	Oxygen.
Phosphorus Trioxide, or Phosphorous oxide	62 +	48
Phosphorus Pentoxide, or Phosphoric oxide	62 +	80

Both these are acid oxides, uniting with water and metallic oxides to form salts, called *phosphites* and *phosphates* respectively; the hydrogen salts being also called *phosphorous* and *phosphoric acid.* There is also another oxygen-acid of phosphorus, containing a smaller proportion of oxygen, called *hypophosphorous acid,* to which there is no corresponding anhydrous oxide.

Hypophosphorous Acid.† — When phosphorus is boiled with a solution of

* In symbols: —
Phosphorous oxide . . . . . P_2O_3
Phosphoric oxide . . . . . P_2O_5.

† Hypophosphorous acid . . . PO_2H_3.

potash or baryta, water is decomposed, giving rise to phosphoretted hydrogen, phosphoric acid, and hypophosphorous acid; the first escapes as gas, and the two acids remain as barium salts.* By filtration the soluble hypophosphite is separated from the insoluble phosphate. On adding to the liquid the quantity of sulphuric acid necessary to precipitate the base, the hypophosphorous acid is obtained in solution. By evaporation it may be reduced to a syrupy consistence. The acid is very prone to absorb more oxygen, and is therefore a powerful deoxidizing agent. All its salts are soluble in water.

Phosphorous Oxide is formed by the slow combustion of phosphorus in the atmosphere; or by burning that substance by means of a very limited supply of dry air, in which case it is anhydrous, and presents the aspect of a white powder. *Phosphorous acid* is most conveniently prepared by adding water to the trichloride of phosphorus, when mutual decomposition takes place, the oxygen of the water being transferred to the phosphorus, generating phosphorous acid, and its hydrogen to the chlorine, giving rise to hydrochloric acid.† By evaporating the solution to the consistence of syrup, the hydrochloric acid is expelled, and the residue, on cooling, crystallizes.

Phosphorous acid is very deliquescent and very prone to attract oxygen and pass into phosphoric acid. When heated in a close vessel, it is resolved into phosphoric acid and pure phosphoretted hydrogen gas. It is composed of 110 parts of phosphorous oxide and 54 parts of water, or, 31 phosphorus, 48 oxygen, and 3 hydrogen.‡

The phosphites are of little importance.

Phosphoric Oxide (also called *Anhydrous Phosphoric Acid*, or *Phosphoric Anhydride*). — When phosphorus is burned under a bell-jar by the aid of a copious supply of dry air, snow-like phosphoric oxide is produced in great quantity. This substance exhibits as much attraction for water as sulphuric oxide: exposed to the air for a few moments, it deliquesces to a liquid, and when thrown into water, combines with the latter with explosive violence. The water then taken up cannot again be separated.

When nitric acid of moderate strength is heated in a retort with which a receiver is connected, and fragments of phosphorus are added singly, taking care to suffer the violence of the action to subside between each addition, the phosphorus is oxidized to its maximum, and converted into phosphoric acid. By distilling off the greater part of the acid, transferring the residue in the retort to a platinum vessel, and then cautiously raising the heat to redness, the acid may be obtained pure. This is the *glacial phosphoric acid* of the Pharmacopœia.

A third method consists in taking the acid calcium phosphate produced by the action of sulphuric acid on bone-earth, precipitating it with a slight excess of ammonia carbonate, separating by a filter the insoluble calcium-salt, and then evaporating and igniting in a platinum vessel the mixed phosphate and sulphate of ammonia. Phosphoric acid alone remains behind. The acid thus obtained is not remarkable for its purity. One of the most advantageous methods of preparing phosphoric acid on the large scale in a state of purity is to burn phosphorus in a stream of dry atmospheric air, by the aid of a proper apparatus, not difficult to contrive, in which the process may be carried on continuously. The phosphoric oxide

* P_3 (Phosphorus.) + $3BaH_2O_2$ (Barium hydrate.) + $6H_2O$ (Water.) = $3BaH_4(PO_2)_2$ (Barium hydrophosphite.) + $2PH_3$ (Hydrogen phosphide.)

† PCl_3 (Phosphorus trichloride.) + $3OH_2$ (Water.) = PO_3H_3 (Phosphorous acid.) + $3HCl$ (Hydrochloric acid.)

‡ $P_2O_3.3OH_2 = 2PO_3H_3$.

obtained may be preserved in that state, or converted into hydrate or glacial acid, by the addition of water and subsequent fusion in a platinum vessel. The glacial phosphoric acid is exceedingly deliquescent, and requires to be kept in a closely stopped bottle. It contains 142 parts of phosphoric oxide and 18 parts of water, or 31 phosphorus, 48 oxygen, and 1 hydrogen.*

Phosphoric oxide is readily volatilized, and may be sublimed by the heat of an ordinary spirit-lamp. The acid may be fused in a platinum crucible at a red heat; at this temperature, it evolves considerable quantities of vapor, but is still far from its boiling-point. Phosphoric acid is a very powerful acid: being less volatile than sulphuric acid, it expels the latter at higher temperatures, although it is displaced by sulphuric acid at the common temperature. Its solution has an intensely sour taste, and reddens litmus-paper; it is not poisonous.

The best reagent for the detection of phosphoric acid is molybdate of ammonia. A solution of this salt is treated with hydrochloric or nitric acid until the precipitate at first formed is redissolved. A very small quantity of the liquid to be tested for phosphoric acid is then added to this solution. If phosphoric acid be present, the liquid becomes yellow, and a yellow deposit, consisting of molybdic acid, phosphoric acid, and ammonia, is formed, even if the quantity of phosphoric acid be very small.

There are few bodies that present a greater degree of interest to the chemist than this substance: the changes its compounds undergo by the action of heat, chiefly made known to us by the admirable researches of Professor Graham, will be described in connection with the general history of saline compounds.

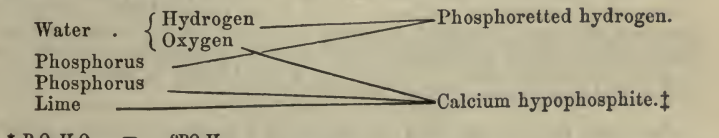
Compounds of Phosphorus and Hydrogen.

Phosphorus Trihydride. — Phosphine. — Phosphoretted Hydrogen. This body is analogous in some of its chemical relations to ammoniacal gas; its alkaline properties are, however, much weaker.

It may be obtained in a state of purity by heating phosphorous acid in a small retort, the acid being then resolved into phosphoretted hydrogen and phosphoric acid.†

Thus obtained, the gas has a density of 1·24. It contains 31 parts phosphorus and 3 parts hydrogen, and is so constituted that every two volumes contain 3 volumes of hydrogen and half a volume of phosphorus vapor, condensed into two volumes. It possesses a highly disagreeable odor of garlic, is slightly soluble in water, and burns with a brilliant white flame, forming water and phosphoric acid.

Phosphoretted hydrogen may also be produced by boiling together, in a retort of small dimensions, caustic potash or slaked lime, water, and phosphorus: the vessel should be filled to the neck, and the extremity of the latter made to dip into the water of the pneumatic trough. In the reaction which ensues, the water is decomposed, and both its elements combine with the phosphorus.



* $P_2O_5.H_2O = 2PO_3H.$

† $4PO_3H_3 = PH_3 + 3PO_4H_3$
Phosphorous acid. Phosphine. Phosphoric acid.

‡ $P_8 + 3CaH_2O_2 + 6OH_2 = 2PH_3 + 3P_2O_4CaH_4$
Phosphorus. Calcium hydrate. Water. Phosphine. Calcium hypophosphite.

The phosphoretted hydrogen prepared by the latter process has the singular property of spontaneous inflammability when admitted into the air or into oxygen gas; with the latter, the experiment is very beautiful, but requires caution: the bubbles should be admitted singly. When kept over water for some time, the gas loses this property, without otherwise suffering any appreciable change; but if dried by calcium chloride, it may be kept unaltered for a much longer time. M. Paul Thénard has shown that the spontaneous combustibility of the gas arises from the presence of the vapor of a liquid hydrogen phosphide, which can be procured in small quantity, by conveying the gas produced by the action of water on calcium phosphide through a tube cooled by a freezing mixture. This substance forms a colorless liquid of high refractive power and very great volatility. It does not freeze at —17·8° (0° F.) In contact with air, it inflames instantly, and its vapor in very small quantity communicates spontaneous inflammability to pure phosphoretted hydrogen, and to all other combustible gases. It is decomposed by light into gaseous phosphoretted hydrogen, and a solid phosphide which is often seen on the inside of jars containing gas which, by exposure to light, has lost the property of spontaneous inflammation. Strong acids occasion its instantaneous decomposition. It is as unstable as hydrogen dioxide. It is to be observed that the pure phosphoretted hydrogen gas itself becomes spontaneously inflammable if heated to the temperature of boiling water.*

Phosphoretted hydrogen decomposes several metallic solutions, giving rise to precipitates of insoluble phosphides. With hydriodic acid it forms a crystalline compound somewhat resembling sal-ammoniac.

Compounds of Phosphorus with Chlorine.

Phosphorus forms two chlorides, analogous in composition to the oxides, the quantities of chlorine combined with the same quantity of phosphorus being to one another in the proportion of 3 to 5.

Phosphorus Trichloride, or Phosphorous Chloride,† is prepared in the same manner as sulphur bichloride, by gently heating phosphorus in dry chlorine gas, the phosphorus being in excess; or by passing the vapor of phosphorus over fragments of calomel (mercurous chloride) contained in a glass tube, and strongly heated. It is a colorless, thin liquid, which fumes in the air, and has a powerful and offensive odor. Its specific gravity is 1.45. Thrown into water, it sinks to the bottom of that liquid, and is slowly decomposed, yielding phosphorous acid and hydrochloric acid.‡ It contains 31 parts phosphorus and 106·5 parts chlorine.

Phosphorus Pentachloride, or Phosphoric Chloride,§ is formed when phosphorus is burned in excess of chlorine. Pieces of phosphorus are introduced into a large tubulated retort, which is then filled with dry chlorine gas. The phosphorus takes fire, and burns with a pale flame, forming a white volatile crystalline sublimate, which is the pentachloride. It may be obtained in larger quantity by passing a stream of dry chlorine gas into the preceding liquid trichloride, which becomes gradually converted into a solid crystalline mass. Phosphorus pentachloride is decomposed by water, yielding phosphoric and hydrochloric acids. ‖

* Ann. Chim. Phys., 3d series, xiv. 5. According to M. P. Thénard, the liquid phosphide of hydrogen contains PH_2 and the solid P_2H. The gas is represented by the formula PH_3.

† PCl_3.

‡ $PCl_3 + 3OH_2 = 3HCl + PO_3H_3$.

§ PCl_5.

‖ $PCl_5 + 4OH_2 = 5HCl + PO_4H_3$.

Phosphorus Oxychloride.*—When phosphorus pentachloride is heated with a quantity of water insufficient to convert it into phosphoric acid, it yields, together with hydrochloric acid, a compound of phosphorus, chlorine, and oxygen. This body may also be prepared by distilling the pentachloride with dehydrated oxalic acid, or by distilling a mixture of phosphorus pentachloride and phosphoric oxide. Phosphorus oxychloride is a colorless liquid of sp. gr. 1·7, possessing a very pungent odor, and boiling at 110° (230° F.). It is readily decomposed by water into hydrochloric and phosphoric acids.

A *sulphochloride*† of analogous composition is produced by the action of hydrogen sulphide on the pentachloride. It is a colorless, oily liquid, decomposed by water.

Two *bromides of phosphorus*, an *oxybromide* and a *sulphobromide*, are known, corresponding in composition and properties with the chlorine compounds, and obtained by similar processes.

Phosphorus forms also two *iodides*,‡ containing 31 parts of phosphorus with 2×127 and 3×127 parts of iodine. The latter is analogous in composition to the trichloride; the former has no chlorine representative. Both these compounds are obtained by dissolving phosphorus and iodine together in carbon bisulphide, and cooling the liquid till crystals are deposited. Whatever proportions of iodine and phosphorus may be used, these two compounds always crystallize out, mixed with excess either of iodine or of phosphorus.

The *di-iodide* melts at 110° (230° F.), forming a red liquid which condenses to a light red solid. The *tri-iodide* melts at 55° (131° F.), and crystallizes on cooling in well defined prisms. Both are decomposed by water, yielding hydriodic and phosphorous acids, the di-iodide also depositing yellow flakes of phosphorus.

Compounds of Phosphorus with Sulphur and Selenium.

Sulphides.—When ordinary phosphorus and sulphur are heated together in the dry state, or melted together under water, combination takes place between them, attended with vivid combustion and often with violent explosion. When amorphous phosphorus is used, the reaction is not explosive, though still very rapid.

Six compounds of sulphur and phosphorus have been prepared, containing the following proportions of sulphur and phosphorus.§

	Composition by weight.		
	Phosphorus.		Sulphur.
Hemisulphide	31	+	8
Monosulphide	31	+	16
Sesquisulphide	31	+	24
Trisulphide	31	+	48
Pentasulphide	31	+	80
Dodecasulphide	31	+	192

The fourth and fifth are analogous to phosphorus and phosphoric oxides respectively; the others have no known analogues in the oxygen series. They may all be formed by heating the two bodies together in the required proportions; but the trisulphide and pentasulphide are more easily prepared by warming the monosulphide with additional proportions of sulphur. Moreover, the two lower sulphides exhibit isomeric modifications, each being capable of existing as a colorless liquid and as a red solid. The

* $POCl_3$. † $PSCl_2$. ‡ PI_2 and PI_3.
§ P_4S, P_2S, P_4S_3, P_2S_3, P_2S_5, and P_2S_{12}.

mono-, tri-, and pentasulphides of phosphorus unite with metallic sulphides, forming sulphur-salts.*

Selenides of Phosphorus, † analogous in composition to the first, second, fourth, and fifth of the sulphides above mentioned, are produced by heating ordinary phosphorus and selenium together in the required proportions in a stream of hydrogen gas. The hemiselenide is a dark-yellow, oily, fetid liquid, solidifying at 12°; the other compounds are dark-red solids. The mono-, tri-, and pentaselenides unite with metallic selenides, forming selenium-salts analogous to the sulphur-salts above mentioned.

* Copper Hyposulphophosphite $P_2S_2Cu = CuS.P_2S$.
Copper Sulphophosphite $P_2S_4Cu = CuS.P_2S_3$.
Copper Sulphophosphate $P_2S_6Cu = CuS.P_2S_5$.

† PSe, P_2Se, P_2Se_3, and P_2Se_5.

ON THE GENERAL PRINCIPLES OF CHEMICAL PHILOSOPHY.

THE study of the non-metallic elements can be pushed to a very considerable extent, and a large amount of precise and exceedingly important information acquired, without much direct reference to the great fundamental laws of chemical union. The subject cannot be discussed in this manner completely, as will be obvious from frequent cases of anticipation in many of the foregoing foot-notes: still, much may be done by this simple method of proceeding. The bodies themselves, in their combinations, furnish admirable illustrations of the general laws referred to; but the study of their leading characters and relations does not of necessity involve a previous knowledge of these laws themselves.

It is thought that by such an arrangement the comprehension of these very important general principles may become, in some measure, facilitated by constant reference to examples of combinations, the elements and products of which have already been described. So much more difficult is it to gain a clear and distinct idea of any proposition of great generality from a simple enunciation, than to understand the bearing of the same law when illustrated by a single good and familiar instance.

Before proceeding further, however, it is absolutely necessary that these matters should be discussed: the metallic compounds are so numerous, that the establishment of some general principle, some connecting link, becomes indispensable. The doctrines of equivalence and combining proportions, and the laws which regulate the formation of saline compounds, supply this deficiency.

THE LAWS OF COMBINATION BY WEIGHT.

(1.) *Constancy of Composition.* — This is the main distinction between chemical combination and mechanical mixture, or that kind of adhesion which gives rise to the solution of a solid in a liquid. Metals may be fused together to form alloys; water may be mixed with alcohol, alcohol with ether, and different oils one with the other, in any proportions whatever, the mixture always exhibiting properties intermediate between those of its constituents, and in regular gradation according to the quantity of each that may be present; a solid body may be dissolved in a liquid — salt or sugar in water, for example — in any proportion up to a certain limit, the solution likewise exhibiting a regular gradation of physical properties, according to the quantity of the solid taken up. But in a true chemical compound, the properties of the constituent elements admit of no variation whatever. Water, whether obtained from natural sources, or formed by direct combination of its elements, always contains in 100 parts, 88·9 parts of oxygen and 11·1 parts of hydrogen; and a piece of flint, or rock-crystal, obtained from any part of the world, invariably contains 46·6 per cent. of silicium to 53·4 of oxygen. When two or more compounds are formed of the same elements, as the oxides of carbon and the chlorides of phosphorus (pp. 164, 216), there is no gradual blending of one into the other, as in the case of mixtures; but each compound is sharply defined and separated, as it were, from the others by an impassable gulf, exhibiting properties dis-

tinct from those of the others, and of the elements themselves in the separate state. Thus of the two oxides of carbon, the monoxide is an inflammable gas, lighter than air, and not absorbed by solution of potash, whereas the dioxide is non-inflammable, heavier than air, and easily absorbed by potash; and both compounds differ entirely in their characters, both from carbon and from oxygen in the free state.

The composition of chemical compounds is ascertained, as already observed, by analysis, and in some cases also by synthesis. The results are usually stated in percentages (thus, 100 parts of zinc oxide contain 80·1 parts zinc and 19·9 oxygen), which for many purposes is as convenient a method as can be adopted. But when it is desired to compare the composition of several compounds of the same elements, or of the compounds formed by one element with several others, it is more convenient to start with a fixed quantity of the first element, and specify the relative quantities of the other element or elements which combine with it. This will be easily seen by comparing the following tabular statements of the composition of the five nitrogen oxides already described, first, in percentages, secondly, by stating the several quantities of oxygen which unite with 100 parts of nitrogen.

	In 100 parts.		With constant quantity of Nitrogen.	
	Nitrogen.	Oxygen.	Nitrogen.	Oxygen.
Monoxide . .	63·64	36·36	100	175
Dioxide . . .	46·67	53·33	100	350
Trioxide . . .	36.85	63·15	100	525
Tetroxide . .	30·44	69·56	100	700
Pentoxide . .	25·93	74·07	100	875

The numbers on the left-hand side of the table do not exhibit any simple relation; but on looking to the right-hand side, it is immediately seen that the quantities of oxygen which unite with the same quantity of nitrogen, are to one another as the numbers 1, 2, 3, 4, 5. And this leads us to the second general law of chemical combination, viz.:

(2.) *The Law of Multiples.* — This law may be thus stated: If two elements, A and B, are capable of uniting in several proportions, the quantities of B which unite with a given quantity of A, usually bear a simple relation to one another, such as:

A + B, A + 2B, A + 3B, A + 4B, &c.;
or, 2A + 3B, 2A + 5B, 2A + 7B, &c.;
or, A + B, A + 3B, A + 5B, &c.

Numerous examples of this law are afforded by the compounds of the non-metallic elements one with the other; as, for example, the oxides of hydrogen, carbon, chlorine, sulphur, and phosphorus, the chlorides of phosphorus, &c.; and still more numerous examples will be met with, in treating of the compounds of metals with non-metallic elements.

It must be observed, however, that more complex relations are by no means unfrequent. The compounds of carbon and hydrogen, for example, are very numerous; and on comparing together the quantities of hydrogen H, which unite with a fixed quantity of carbon C, we meet with such relations as 5C + 17H, 7C + 16H, 11C + 24H, 15C + 32H, &c. In short, the simple relations above mentioned must be looked upon merely as particular instances of a large number of possible relations, although they happen to hold good with reference to a considerable number of important compounds.

(3.) *Law of Equivalents.* — If a body A unites with certain other bodies B, C, D, then the quantities B, C, D, which combine with A, or certain simple multiples of them, represent for the most part the proportions in which they can unite amongst themselves.

For example, 8 parts by weight of oxygen are known to unite with the following quantities of hydrogen, nitrogen, &c.:

Oxygen	8
Hydrogen	1
Nitrogen	14
Carbon	6
Sulphur	8
Phosphorus	$10\frac{1}{3}$ or $\frac{31}{3}$
Chlorine	35·5
Iodine	$25\frac{2}{5}$ or $\frac{127}{5}$
Potassium	39
Iron	28
Copper	31·7
Lead	103·5
Silver	108
&c.	&c

And it is found, moreover, that hydrogen and chlorine combine in the proportions 1 to 35·5; hydrogen and sulphur, 1 to 2×8; chlorine and silver, 35·5 to 108; iodine and potassium, 127 parts of the former to 39 of the latter, &c.; phosphorus and chlorine, 31 parts of the former to $3\times35{\cdot}5$ and $5\times35{\cdot}5$ of the latter, &c.

Now, on comparing the relative quantities of the elements contained in all known chemical compounds, it is found: 1. That there is a certain number of elements which combine with one another in one proportion only. 2. That by far the greater number of elements are capable of uniting in two or more proportions. The elements of the former class may be conveniently called *monogens*, those of the latter *polygens*.*

Hydrogen and chlorine unite in the proportion of 1 part, by weight, of the former, to 35·5 parts of the latter, and in no other. The same quantity of chlorine combines with 39·1 parts of potassium, 23 of sodium, and 108 of silver. These several quantities of sodium, potassium, and silver, are capable of saturating the same quantity of chlorine that is saturated by 1 part of hydrogen. They are, therefore, in this respect *equivalent* to 1 part by weight of hydrogen and to each other. They may, in fact, be made directly to replace one another in combination with chlorine. Thus, when sodium or potassium is heated in hydrochloric acid gas, hydrogen is set free, and sodium or potassium chloride is formed, 23 parts of sodium or 39·1 parts of potassium always taking the place of 1 part of hydrogen. Again, when a solution of sodium chloride is mixed with silver nitrate, the sodium and silver change places, forming a solution of sodium nitrate and a precipitate of silver chloride; and in this case 108 parts of silver take the place of 23 parts of sodium. The above-mentioned quantities of hydrogen, chlorine, sodium, potassium, and silver, are therefore called *equivalent weights*.

There are a few other monogenic elements, the names and equivalent weights of which are given, together with the preceding, in the following table:

* Erlenmeyer, "Lehrbuch der organischen Chemie."

Hydrogen	1	Potassium	39·1
Chlorine	35·5	Sodium	23
Bromine	80	Lithium	7
Fluorine	19	Cæsium	133
Silver	108	Rubidium	85·4

All other elements are polygenic, uniting with the monogens and with one another in more than one proportion. With regard to these elements the question of equivalence appears at first to be somewhat indeterminate; in fact, according to the idea of equivalency above defined, the equivalent value of a polygenic element must vary according to the proportions in which it unites with others. Thus iron forms two chlorides, containing 28 and 18⅔ parts of iron to 35.5 parts of chlorine. Either of these quantities of iron may therefore be regarded as equivalent to 1 part of hydrogen; in other words, as the equivalent weight of iron. Again, 1 part of hydrogen unites with 8 parts of oxygen to form water, and with 16 parts to form hydrogen dioxide. Which of these is the equivalent weight of oxygen? The former number has perhaps the best right to be so regarded, because water is a more stable compound than hydrogen-dioxide, and, moreover, 8 parts by weight of oxygen frequently take the place of 1 part of hydrogen in processes of oxidation, as when alcohol, a compound of 12 parts carbon, 3 hydrogen, and 8 oxygen, is oxidized to acetic acid, containing 12 parts carbon, 2 hydrogen, and 16 oxygen. But what number shall we fix upon as the equivalent of nitrogen? This element forms only one compound with hydrogen, namely, ammonia, which contains 14 parts of nitrogen to 3 of hydrogen, or 4⅔ nitrogen to 1 hydrogen. Accordingly, the equivalent weight of nitrogen appears to be 4⅔, and, in fact, this quantity of nitrogen can be made to take the place of 1 part of hydrogen in many organic compounds. But if we look to the compounds of nitrogen with oxygen, we find that these elements unite in five different proportions, 8 parts of oxygen (which we have seen to be in most cases equivalent to 1 part of hydrogen) uniting with 14, 7, ¼, ½, or ⅕ parts of nitrogen, either of which numbers may therefore be regarded as equivalent to 1 part of hydrogen. Lastly, with regard to carbon, the problem appears still more indefinite, inasmuch as that element forms with hydrogen a very large number of compounds, and appears to be capable of uniting with it in almost any proportion.

We may, however, obtain a set of comparable values by assuming as the equivalent weight of each polygenic element, the *smallest quantity* of it which unites with 1 part of hydrogen, or with 35·5 of chlorine, or generally with the equivalent weight of any monogenic element. Thus of all the compounds of hydrogen and carbon, marsh-gas, or methane, which is composed of 12 parts carbon to 4 hydrogen, or 3 parts carbon to 1 hydrogen, contains the largest quantity of hydrogen in proportion to the carbon; in other words, 3 parts of carbon is the smallest quantity that can unite with 1 part of hydrogen This, then, we shall regard as the equivalent weight of carbon; and by similar considerations the equivalent weight of oxygen will be found to be 8, that of sulphur 16, of nitrogen 4⅔ or ¼, of phosphorus ⅜ or 6⅕, of iron 18⅔, of lead 103·5, &c.

Atomic Weights.—Let us now compare the hydrogen compounds of monogenic and polygenic elements, with regard to the manner in which the hydrogen contained in them may be replaced by other elements. Compare first hydrochloric acid and water. When hydrochloric acid is acted upon by certain metals, as sodium, zinc, or magnesium, *the whole* of the hydrogen is expelled, and the chlorine enters into combination with an equivalent quantity of the metal; thus 36·5 parts of hydrochloric acid (= 1 part hydrogen + 35·5 chlorine) and 23 sodium yield 1 part of free

hydrogen and 23 + 35·5 (= 58·5) sodium chloride; there is no such thing as the expulsion of *part* of the hydrogen, or the formation of a compound containing both hydrogen and metal in combination with the chlorine.

With water, however, the case is different. When sodium is thrown upon water, 9 parts of that compound (= 1 hydrogen + 8 oxygen) are decomposed, in such a manner that half of the hydrogen is expelled by an equivalent quantity of sodium, $\frac{23}{2}$, and *sodium hydrate* is formed containing:—

Sodium.		Hydrogen.		Oxygen.
$\frac{23}{2}$	+	$\frac{1}{2}$	+	8

This compound remains in the solid state when the liquid is evaporated to dryness; and if it be further heated in a tube with sodium, the remaining half of the hydrogen is driven off, and anhydrous sodium-oxide remains, composed of 23 parts sodium + 8 oxygen.

Water differs, therefore, from hydrochloric acid in this respect, that its hydrogen may be replaced by a monogenic metal in two equal portions, yielding successively a hydrate and an anhydrous oxide, the relations of which to the original compound may be thus represented:—

Water.		Sodium-hydrate.		Sodium-oxide.
Hydrogen. Oxygen.		Hyd. Sod. Ox.		Sodium. Ox.
$\left(\frac{1}{1}+\frac{1}{2}\right)$	+ 8	$\left(\frac{1}{2}+\frac{23}{2}\right)$	+ 8	$\left(\frac{23}{2}+\frac{24}{2}\right)$ + 8;

or, multiplying by 2, to avoid fractions of equivalent weights:

Water.		Sodium-hydrate.		Sodium-oxide.
Hydrogen. Oxygen.		Hyd. Sod. Ox.		Sodium. Ox.
(1 + 1)	+ 16	(1 + 23)	+ 16	(23 + 23) + 16.

It appears from this that 2 × 8, or 16 parts of oxygen, is the smallest quantity of oxygen that can be supposed to enter into the reaction just considered, if we would avoid speaking of fractions of equivalents; and we shall find hereafter that the same is true with regard to all other well-defined reactions in which oxygen takes part. Hence this quantity of oxygen 16 parts by weight (hydrogen being the unit), is called an *indivisible* weight, or *atomic weight*, or an *atom* of oxygen.*

Let us now consider the hydrogen compound of nitrogen, that is to say, *ammonia*. This is composed of 1 part of hydrogen united with $4\frac{2}{3}$ or $\frac{14}{3}$ of nitrogen. Now in this compound the hydrogen is replaceable by thirds. When potassium is heated in ammonia gas, a compound called *potassamine* is formed, in which one third of the hydrogen is replaced by potassium. Another compound, called *tri-potassamine*, is also known, consisting of ammonia in which the whole of the hydrogen is replaced by an equivalent quantity of potassium:—

	Nit.	Hydrogen.				Nit.	Hydrogen.		
Ammonia . .	$\frac{14}{3}$	+ $\frac{1}{3}$	+ $\frac{1}{3}$	+ $\frac{1}{3}$	or	14	+ 1	+ 1	+ 1
	Nit.	Hydrogen.		Pot.		Nit.	Hydrogen.		Pot.
Potassamine .	$\frac{14}{3}$	+ $\frac{1}{3}$	+ $\frac{1}{3}$	+ $\frac{39}{3}$	or	14	+ 1	+ 1	+ 39
	Nit.	Potassium.				Nit.	Potassium.		
Tripotassamine	$\frac{14}{3}$	+ $\frac{39}{3}$	+ $\frac{39}{3}$	+ $\frac{39}{3}$	or	14	+ 39	+ 39	+ 39

* Ἄτομος, indivisible.

There is also a large class of compounds derived from ammonia in like manner by the replacement of $\frac{1}{3}$, $\frac{2}{3}$, or the whole of the hydrogen by equivalent quantities of certain groups of elements called *compound radicals* (see page 237). Hence, by reasoning similar to that which was above applied to water, it is inferred that ammonia is composed of 14 parts by weight, or 3 equivalents, of nitrogen combined with 3 parts or 3 equivalents of hydrogen, and that the atomic weight of nitrogen is 14.

Next take the case of *marsh-gas* or *methane*, a compound of 1 part hydrogen with 3 parts carbon. When this gas is mixed with chlorine, and exposed to diffused daylight, a new compound is formed, in which one fourth of the hydrogen belonging to the marsh-gas is replaced by an equivalent quantity of chlorine; and if the chlorine is in excess, and the mixture exposed to sunshine, three other compounds are formed, in which one half, three fourths, and all the hydrogen, are thus replaced. The results may be thus expressed:

Methane.

Carbon. Hydrogen. Carbon. Hydrogen.

$$3 + \tfrac{1}{4} + \tfrac{1}{4} + \tfrac{1}{4} + \tfrac{1}{4} \text{ or } 12 + 1 + 1 + 1 + 1$$

Chloromethane.

Carbon. Hydrogen. Chlorine. Carbon. Hydrogen. Chlorine.

$$3 + \frac{1}{4} + \frac{1}{4} + \frac{1}{4} + \frac{35{\cdot}5}{4} \text{ or } 12 + 1 + 1 + 1 + 35{\cdot}5$$

Dichloromethane.

Carbon. Hydrogen. Chlorine. Carbon. Hydrogen. Chlorine.

$$3 + \frac{1}{4} + \frac{1}{4} + \frac{35{\cdot}5}{4} + \frac{35{\cdot}5}{4} \text{ or } 12 + 1 + 1 + 35{\cdot}5 + 35{\cdot}5$$

Trichloromethane or Chloroform.

Carbon. Hyd. Chlorine. Carb. Hyd. Chlorine.

$$3 + \frac{1}{4} + \frac{35{\cdot}5}{4} + \frac{35{\cdot}5}{4} + \frac{35{\cdot}5}{4} \text{ or } 12 + 1 + 35{\cdot}5 + 35{\cdot}5 + 35{\cdot}5$$

Tetrachloromethane.

Carbon. Chlorine. Carbon. Chlorine.

$$3 + \frac{35{\cdot}5}{4} + \frac{35{\cdot}5}{4} + \frac{35{\cdot}5}{4} + \frac{35{\cdot}5}{4} \text{ or } 12 + 35{\cdot}5 + 35{\cdot}5 + 35{\cdot}5 + 35{\cdot}5$$

Hence, by reasoning similar to the above, it is inferred that marsh-gas is composed of 12 parts by weight, or 4 equivalents of carbon, and 4 parts, or 4 equivalents of hydrogen, and that the atomic weight of carbon is 12.

According to the preceding explanations, the *equivalent weight* of a polygenic element is the smallest quantity of it that can unite with an equivalent of a monogenic element, that is, with 1 part of hydrogen, 35·5 parts of chlorine, &c.; and the *atomic weight*, or *atom*, is the smallest quantity of an element that can unite with others without introducing fractions of equivalents. In the case of a monogenic element, the atomic and equivalent weights are identical, but the atomic weight of a polygenic element is always greater than the equivalent weight in the ratio of 1 to 2, 3, 4, &c.

We have shown in three cases how the atomic weight of an element may be determined by the proportion in which equivalent substitution takes place in its compounds with hydrogen or other monogenic elements. Sulphur, selenium, and tellurium form hydrogen compounds exactly analogous in this respect to water, the hydrogen being replaceable by halves; their atomic weights are therefore double of their equivalent weights. Silicon forms with chlorine a compound containing 7 parts silicon with 35·5 parts chlorine; and in this one fourth of the chlorine is replaceable by hydrogen or by bromine: hence the atomic weight of silicon is, like that of carbon, equal to four times the equivalent weight, its numerical value being 28. There are also some elements in which the atomic weight is equal to five times, and others in which it is equal to six times, the equivalent weight; higher ratios have not been observed.

It must not be supposed that the atomic weights of elementary bodies are always actually determined in the manner above described. There are several other methods of determining their numerical values, as will be presently explained; and the values obtained by different methods do not always agree; but the atomic weights of all the more important elements may be regarded as definitely fixed within small numerical errors. The equivalent value of an element or the ratio of the equivalent to the atomic weight, is also subject to some variation, as will be presently explained, according to the view which may be taken of the constitution of particular compounds.

The table on the next page exhibits the values of the atomic weights of the elementary bodies in which chemists are now for the most part agreed; also the abbreviated symbols (the first or first two letters of their Latin names) by which they are designated in chemical formulæ.

Symbolic Notation. — The symbols, H, O, N, etc., stand, not for the names of the several elements, but for quantities of them proportional to the atomic weights. Combination between elements is represented by the juxtaposition of the symbols; thus NaCl represents sodium chloride, a compound of 23 parts by weight of sodium with 36·5 parts of chlorine. Two or more atoms of an element are represented by placing a small figure to the right of the symbol, and a little below; thus H_2 denotes 2 atoms of hydrogen; OH_2 denotes water, a compound of 2 atoms hydrogen with 1 atom oxygen; PCl_5, phosphorus pentachloride; Fe_2O_3, iron sesquioxide, etc. The elements in a compound are usually placed in the order of their equivalencies, the highest to the left; but this order is often departed from when, by so doing, the relation between two or more compounds under consideration can be more clearly brought to light.

The union of two atomic groups, or *molecules*, is represented by placing their symbols together, with a point or comma between them; thus sal-ammoniac, formed by the union of ammonia, NH_3, and hydrochloric acid, HCl, is represented by the formula $NH_3.HCl$; sulphuric acid, or hydrogen sulphate, which may be regarded as sulphur trioxide combined with water, may be represented by the formula $SO_3.OH_2$.

A number placed to the left of a group of symbols not separated by a point or comma, multiplies the entire group; thus $3OH_2$ denotes 3 molecules of water; but to denote the multiplication of a molecule compounded of two other molecules, the whole formula must be enclosed in brackets, and the numeral placed to the left on the line, or to the right a little below it; thus 2 molecules of sal-ammoniac are denoted by $2(NH_3.HCl)$, or $(NH_3\ HCl)_2$.

If the brackets were omitted in the first of these formulæ, the 2 would multiply only the part of the formula to the left of the point; *e. g.* $3OH_2.SO_3$

TABLE OF ELEMENTARY BODIES WITH THEIR SYMBOLS AND ATOMIC WEIGHTS.

Name.	Symbol.	Atomic Weight.	Name.	Symbol.	Atomic Weight.
Aluminium	Al	27·4	Molybdenum	Mo	96
Antimony (Stibium)	Sb	122	Nickel	Ni	58·8
Arsenic	As	75	Niobium	Nb	94
Barium	Ba	137	Nitrogen	N	14
Beryllium	Be	9·4	Osmium	Os	199·2
Bismuth	Bi	210	Oxygen	O	16
Boron	B	11	Palladium	Pd	106·6
Bromine	Br	80	Phosphorus	P	31
Cadmium	Cd	112	Platinum	Pt	197·4
Cæsium	Cs	133	Potassium (Kalium)	K	39·1
Calcium	Ca	40	Rhodium	Rh	104·4
Carbon	C	12	Rubidium	Rb	85·4
Cerium	Ce	92	Ruthenium	Ru	104·4
Chlorine	Cl	35·5	Selenium	Se	79·4
Chromium	Cr	52·2	Silicium	Si	28
Cobalt	Co	58·8	Silver (Argentum)	Ag	108
Copper (Cuprum)	Cu	63·4	Sodium (Natrium)	Na	23
Didymium	D	95	Strontium	Sr	87·6
Erbium	E	112·6	Sulphur	S	32
Fluorine	F	19	Tantalum	Ta	182
Gold (Aurum)	Au	197	Tellurium	Te	128
Hydrogen	H	1	Terbium (?)		
Indium	In	74	Thallium	Tl	204
Iodine	I	127	Thorinum	Th	115·7
Iridium	Ir	198	Tin (Stannum)	Sn	118
Iron (Ferrum)	Fe	56	Titanium	Ti	50
Lanthanum	La	93·6	Tungsten, or Wolfram	W	184
Lead (Plumbum)	Pb	207	Uranium	U	120
Lithium	Li	7	Vanadium	V	51·2
Magnesium	Mg	24	Yttrium	Y	61·7
Manganese	Mn	55	Zinc	Zn	65·2
Mercury (Hydrargyrum)	Hg	200	Zirconium	Zr	89·6

denotes a compound of 3 molecules of water with 1 molecule of sulphur trioxide.

Chemical reactions are represented by equations, in which the symbols of the acting bodies are placed on the left-hand side, and those of the bodies formed by the reaction, on the right hand, the molecules on either side being connected by the sign +. For example, the action of zinc on hydrochloric acid, by which zinc chloride and free hydrogen are formed, is represented by the equation:

$$Zn + 2HCl = ZnCl_2 + H_2;$$

that of phosphorus pentachloride on water, which yields hydrochloric and phosphoric acids, by the equation:

$$PCl_5 + 4OH_2 = 5HCl + PO_4H_3.$$

Numerous other examples will be found in the foot-notes to the preceding pages.

Physical and Chemical Relations of Atomic Weights.

We have hitherto regarded the atomic weights of the elements as mere numerical expressions, or as quantities adopted to represent the composition of compounds without introducing fractions of equivalents. If this were all that could be said about them, they would not be of much importance. We shall see, however, that these same quantities exhibit some remarkable relations to the physical properties of the elements, and to the proportions in which they combine together by volume.

1. *To the Specific Heat of the Elementary Bodies.*—The atomic weights of the elements, determined according to their modes of combination, are, for the most part, inversely proportional to their specific heats; so that the product of the specific heat into the atomic weight is a constant quantity. The same quantity of heat is required to produce a given change of temperature in 7 grams of lithium, 56 of iron, 207 of lead, 108 of silver, 196·7 of gold, 210 of bismuth, &c.

This relation, already pointed out in the chapter on Heat (p. 73), holds good with respect to the greater number of the elements; but it cannot be regarded as a universal law, inasmuch as three elements, carbon, silicium, and boron, whose atomic weights are well established on chemical grounds, exhibit unmistakable exceptions to it. Nevertheless, in case of doubt as to the correct determination of the atomic weight of an element according to its mode of combination, the agreement of the value thus obtained with the value determined according to the specific heat, is generally regarded as affording strong evidence in favor of the result.

2. *To the Crystalline Forms of Compounds.*—It is found that, in many cases, two or more compounds which, from chemical considerations, are supposed to contain equal numbers of atoms of their respective elements, crystallize in the same or in very similar forms. Such compounds are said to be *isomorphous.** Thus the sulphates represented by the general formula SO_4M_2 (M denoting a monogenic metal) are isomorphous with the corresponding selenates SeO_4M_2; the phosphates PO_4M_3 are isomorphous with the corresponding arsenates AsO_4M_3, &c.

Accordingly, these isomorphous relations are often appealed to for the purpose of fixing the constitution of compounds, and thence deducing the atomic weights of their elements, in cases which would otherwise be doubtful. Thus aluminium forms only one oxide, viz., alumina, which is composed of 18·2 parts by weight of aluminium and 16 parts of oxygen. What, then, is the atomic weight of aluminium? The answer to this question will depend upon the constitution assigned to alumina, whether it is a monoxide, sesquioxide, dioxide, &c. Thus:

			O.		Al.
Monoxide .	AlO	=	16	+	18·25
Sesquioxide	Al_2O_3	=	48	+	27·4 27·4
Dioxide .	AlO_2	=	32	+	36·5
Trioxide .	AlO_3	=	48	+	54·8

The numbers in the last column of this table are the weights which must be assigned to the atom of aluminium, according to the several modes of constitution indicated in the first column; but there is nothing in the con-

* Ἴσος, equal; μορφή, form.

stitution of the oxide itself that can enable us to decide between them. Now, iron forms two oxides, in which the quantities of oxygen united with the same quantity of iron are to one another as 1 : $1\frac{1}{2}$, or as 2 : 3. These are therefore regarded as monoxide, FeO, and sesquioxide, Fe_2O_3, and this last oxide is known to be isomorphous with alumina. Consequently alumina is also regarded as a sesquioxide, Al_2O_3, and the atomic weight of aluminium is inferred to be 27·4.

3. *To the Volume-Relations of Elements and Compounds.*—The atomic weights of those elements which are known to exist in the state of gas or vapor are, with one or two exceptions, proportional to their specific gravities in the same state. Taking the specific gravity of hydrogen as unity, those of the following gases and vapors are expressed by numbers identical with their atomic weights:

Hydrogen	1	Oxygen	16
Chlorine	35.5	Sulphur	32
Bromine	80	Selenium	79
Iodine	127	Tellurium	128

The exceptions to this rule are exhibited by *phosphorus* and *arsenic*, whose vapor-densities are twice as great as their atomic weights, that of phosphorus being 62, and that of arsenic 150; and by *mercury* and *cadmium*, whose vapor-densities are the halves of their atomic weights, that of mercury being 100, and that of cadmium 56.

Laws of Combination by Volume.—From the preceding relations, it follows that the volumes of any two elementary gases which make up a compound molecule, are to one another in the same ratio as the numbers of atoms of the same elements which enter into the compound, excepting in the case of phosphorus and arsenic, for which the number of volumes thus determined has to be halved, and of mercury and cadmium, for which it must be doubled; thus:

The molecule	HCl	contains	1 vol.	H	and	1 vol.	Cl.
"	H_2O	"	2 "	H	"	1 "	O.
"	H_3N	"	3 "	H	"	1 "	N.
"	H_3P	"	3 "	H	"	$\frac{1}{2}$ "	P.
			or 6 "	H	"	1 "	P.
"	Cl_3As	"	3 "	Cl	"	$\frac{1}{2}$ "	As.
			or 6 "	Cl	"	1 "	As.
"	Cl_2Hg''	"	2 "	Cl	"	2 "	Hg.

If the smallest volume of a gaseous element that can enter into combination be called the combining volume of that element, the law of combination may be expressed as follows: *The combining volumes of all elementary gases are equal, excepting those of phosphorus and arsenic, which are only half those of the other elements in the gaseous state, and those of mercury and cadmium, which are double those of the other elements.*

It appears, then, that in all cases the volumes in which gaseous elements combine together may be expressed by very simple numbers. This is the "Law of Volumes," first observed by Humboldt and Gay-Lussac in 1805, with regard to the combination of oxygen and hydrogen, and afterwards established in other cases by Gay-Lussac, whose observations, published in his "Theory of Volumes," afforded new and independent evidence of the combination of bodies in definite and multiple proportions, in corroboration of that derived from the previously observed proportions of combination by weight.

Gay-Lussac likewise observed that the product of the union of two gases,

when itself a gas, sometimes retains the original volume of its constituents, no contraction or change of volume resulting from the combination, but that when contraction takes place, which is the most common case, the volume of the compound gas always bears a simple ratio to the volumes of its elements; and subsequent observation, extended over a very large number of compounds, organic as well as inorganic, has shown that, with a few exceptions, probably only apparent, *the molecules of compound bodies in the gaseous state occupy twice the volume of an atom of hydrogen gas.* No matter what may be the number of atoms or volumes that enter into the compound, they all become condensed into two volumes, thus:

1 vol.	H	and 1 vol.	Cl	form 2 vol.	HCl, hydrochloric acid.
1 "	N	" 1 "	O	" 2 "	NO, nitrogen dioxide.
2 "	H	" 1 "	O	" 2 "	H_2O, water.
3 "	H	" 1 "	N	" 2 "	H_3N, ammonia.
3 "	H	" $\frac{1}{2}$ "	P	" 2 "	H_3P, hydrogen phosphide.

Similarly in the union of compound gases, *e. g.*

1 vol.	ethyl, C_2H_5,	and 1 vol.	Cl,	form 2 vol.	C_2H_5Cl,	ethyl chloride.
2 "	ethyl, C_2H_5,	" 1 "	O	" 2 "	$(C_2H_5)_2O$,	ethyl oxide.
2 "	ethene, C_2H_4,	" 2 "	Cl	" 2 "	$C_2H_4Cl_2$,	ethene chloride.
2 "	ethene, C_2H_4,	" 1 "	O	" 2 "	C_2H_4O,	ethene oxide.

Hence it follows that *the specific gravity of any compound gas or vapor, referred to hydrogen as unity, is equal to half its atomic or molecular weight.*

The quotient obtained by dividing the molecular weight of a body by its specific gravity is called its *Specific* or *Atomic volume;* hence the law just stated may also be thus expressed: *The specific volumes of compound gases or vapors referred to that of hydrogen as unity are, with a few exceptions, equal to* 2. We shall presently show that the same law applies to the specific volumes of the elementary gases themselves.

For many years past, attempts have been made to extend to solids and liquids the results of Gay-Lussac's discovery of the law of gaseous combination by volume, the specific volumes of the bodies in question being determined by the method pursued in the case of gases — namely, by dividing the molecular weight by the specific gravity. The numbers obtained in this manner, representing the specific volumes of the various solid and liquid elementary substances, present far more cases of discrepancy than of agreement. The latter are, however, sufficiently numerous to excite great interest in the investigation. Some of the results pointed out are exceedingly curious as far as they go, but are not as yet sufficient to justify any general conclusion. The inquiry is beset with many great difficulties, chiefly arising from the unequal expansion of solids and liquids by heat, and the great differences of physical state, and, consequently, of specific gravity, often presented by the former.

THE ATOMIC THEORY.

The laws of chemical combination, and the relations between atomic and equivalent weights above explained, are the result of pure experimental inquiry, and independent of all hypothesis. In this, however, as in other branches of science, the comprehension of experimental results may be greatly facilitated by endeavoring to refer them to a general law or mode of action. That no attempt should be made to explain the manner in which

chemical compounds are formed, and to point out the nature of the relations between the different modifications of matter which determine chemical changes, would, indeed, be contrary to the speculative tendency of the human mind. Such an attempt — and a very ingenious and successful one it is — has, in fact, been made, namely, the atomic hypothesis of Dr. Dalton.

From very ancient times, the question of the constitution of matter with respect to divisibility has been debated, some adopting the opinion that this divisibility is infinite, and others, that when the particles become reduced to a certain degree of tenuity, far, indeed, beyond any state that can be reached by mechanical means, they cease to be further diminished in magnitude; they become, in short, *atoms*.* Now, however the imagination may succeed in figuring to itself the condition of matter on either view, it is hardly necessary to mention that we have absolutely no means at our disposal for deciding such a question, which remains at the present day in the same state as when it first engaged the attention of the Greek philosophers, or perhaps that of the sages of Egypt and Hindostan long before them.

Dalton's hypothesis sets out by assuming the existence of such atoms or indivisible particles, and states, that compounds are formed by the union of atoms of different bodies, one to one, one to two, &c. The compound atom, or molecule, joins itself in the same manner to a compound atom of another kind, and a combination of the second order results. Let it be granted, further, that the atoms of different elements have different weights, fixed and invariable for each, and the hypothesis becomes capable of rendering consistent and satisfactory reasons for all the observed numerical laws of chemical combination.

Chemical compounds must always be definite; they must always contain the same number of atoms of the same kind arranged in a similar manner. The same kind and number of atoms need not, however, of necessity produce the same substance, for they may be differently arranged; and much depends upon this circumstance.

Again, the law of multiple proportions is perfectly well explained. One atom of carbon unites with one atom of oxygen to form carbon monoxide, and with two atoms to form carbon dioxide; one atom of sulphur with two and three atoms of oxygen to form the dioxide and trioxide of sulphur; one atom of phosphorus with three and five atoms of chlorine to form the trichloride and pentachloride of phosphorus; two atoms of nitrogen with one, two, three, four and five atoms of oxygen to form the five oxides already mentioned (pp. 157, 220).

The atomic hypothesis likewise affords an easy explanation of the manner in which bodies replace or may be substituted one for the other. Here, however, we come upon an extension of the original Daltonian hypothesis. It was formerly supposed that when one element replaced another in combination, the substitution always took place atom for atom; and accordingly the terms "atoms" and "equivalent" were regarded as synonymous, at least so far as numerical value was concerned. But, according to the atomic weights now adopted, and determined by the considerations above explained, we must suppose that one atom of an element may take the place of two, three, four atoms, &c., of another. It is only, in fact, the atoms of monogenic elements that can replace each other one by one: an atom of a polygenic element, on the other hand, always takes the place of, or is equivalent to, two or more atoms of a monogenic element.

This difference of equivalent or saturating power is often denoted by placing dashes or Roman numerals to the right of the symbol of an element, and at the top, as O'', B''', C^{iv}, &c.; and the several elements are designated as

* Ἄτομος, that which cannot be cut.

Univalent elements,	or	Monads,	as H
Bivalent	"	Dyads	" O″
Trivalent	"	Triads	" B‴
Quadrivalent	"	Tetrads	" C^{iv}
Quinquivalent	"	Pentads	" P^{v}
Sexvalent	"	Hexads	" W^{vi}

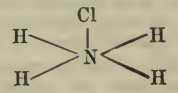
Elements of even equivalency, viz., the dyads, tetrads, and hexads, are also included under the general term *artiads*,* and those of uneven equivalency, viz., the monads, triads, and pentads, are designated generally as *perissads*.†

Another method of indicating the equivalent values of the elementary atoms, and the manner in which they are satisfied by combination, is to arrange the symbols in diagrams in which each element is connected with others by a number of lines, or connecting bonds, corresponding to its degree of equivalence; ‡ a monad being connected with other elements by only one such bond, a triad by three, a hexad by six, &c., as in the following examples: —

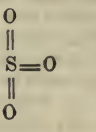
Water, OH_2 . . . . . H—O—H

Carbon dioxide, CO_2 . . . . . O=C=O

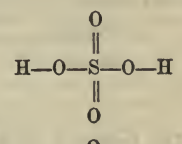
Ammonium chloride, NH_4Cl . . .



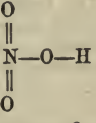
Sulphuric oxide, SO_3. . . . . .



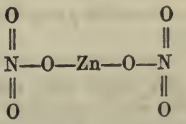
Sulphuric acid, SO_4H_2 . . . .



Nitric acid, NO_3H . . . . .



Zinc nitrate, N_2O_6Zn . . . . .



It must be distinctly understood that these formulæ — which may be called *constitutional formulæ* — are not intended to represent the actual arrangement

* Ἄρτιος, even. † Περισσός, uneven.

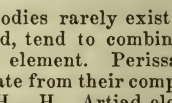
‡ The symbols of the elements in these diagrams are often enclosed in circles to represent the atoms, with rays diverging from them to indicate the number of connecting bonds; such formulæ are called *graphic formulæ*; but the circles do not add anything to the clearness of the representation, and may as well be omitted. For lecture and class illustration, solid diagrams are constructed, with wooden balls of various colors, to represent the atoms, having holes for the insertion of connecting rods; these representations are called *glyptic formulæ*.

of the atoms in a compound; indeed, even if we had a distinct notion of the manner in which the atoms of any compound are arranged, it could not be adequately represented on a plane surface. The lines connecting the different atoms indicate nothing more than the number of units of equivalency belonging to the several atoms, and the manner in which they are disposed of by combination with those of other atoms. Thus the formula for nitric acid indicates that two of the three constituent oxygen-atoms are combined with the nitrogen alone, and are consequently attached to that element by both their units of equivalency, whereas the third oxygen-atom is combined both with nitrogen and with hydrogen.

By inspection of the preceding diagrams, it will be observed that every atom of a compound has each of its units of equivalency satisfied by combination with a unit belonging to some other atom. Such, indeed, is the case in every saturated or normal compound. Accordingly, it is found that in all such compounds the sum of the perissad elements is always an even number. Thus a compound may contain two, four, six, &c., monad atoms, as HCl, OH_2, CH_4, C_2H_6, C_3H_8, SiH_3Cl; or one monad and one triad atom, as BCl_3; or one pentad and five monads, as NH_4Cl; but never an uneven number of perissad atoms. This is the "law of even numbers" announced some years ago by Gerhardt and Laurent as a result of observation. It was long received with doubt, but has now been confirmed by the analysis of so many well-defined compounds, that a departure from it is looked upon as a sure indication of incorrect analysis.

For a similar reason, the atoms of elementary bodies rarely exist in the free state, but, when separated from any compound, tend to combine with other atoms, either of the same or of some other element. Perissad elements, like hydrogen, chlorine, nitrogen, &c., separate from their compounds in pairs; their molecule contains two atoms, *e. g.* H —H. Artiad elements may unite in groups of two, three, or more; thus the molecule of oxygen, in its ordinary state, probably, contains two atoms, that of ozone three atoms; thus:

Oxygen . . . . . O=O

Ozone . . . . . 

The tendency of elementary atoms to separate in groups is shown in various ways. Thus when copper hydride, Cu_2H_2 (to be hereafter described), is decomposed by hydrochloric acid, a quantity of hydrogen is given off equal to twice that which is contained in the hydride itself; thus:

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2HH.$$

This action is precisely analogous to that of hydrochloric acid on cuprous oxide:

$$Cu_2O + 2HCl = Cu_2Cl_2 + OH_2.$$

In the latter case, the hydrogen separated from the hydrochloric acid unites with oxygen, in the former with hydrogen. Again, when solutions of sulphurous acid and sulph-hydric acid are mixed, the whole of the sulphur is precipitated:

$$SO_3H_2 + 2SH_2 = 3OH_2 + S.S_2$$

the action being similar to that of sulphurous acid on selenhydric acid:

$$SO_3H_2 + 2SeH_2 = 3OH_2 + S.Se_2.$$

In the one case, a sulphide of selenium is precipitated; in the other, a sulphide of sulphur. The precipitation of iodine, which takes place on

mixing hydriodic acid with iodic acid, affords a similar instance of the combination of homogeneous atoms:

$$\underset{\text{Hydriodic acid.}}{5IH} + \underset{\text{Iodic acid.}}{IO_3H} = \underset{\text{Water.}}{3OH_2} = \underset{\text{Free iodine.}}{3I}$$

Another striking illustration of this mode of action is afforded by the reduction of certain metallic oxides by hydrogen dioxide. When silver oxide is thrown into this liquid, water is formed; the silver is reduced to the metallic state, and a quantity of oxygen is evolved equal to twice that which is contained in the silver oxide:

$$\underset{\text{Silver oxide.}}{OAg_2} + \underset{\text{Hydrogen dioxide.}}{O_2H_2} = \underset{\text{Water.}}{OH_2} + \underset{\text{Silver.}}{Ag_2} + \underset{\text{Oxygen.}}{OO}$$

Further, elementary bodies frequently act upon others as if their atoms were associated in binary groups. Thus, chlorine acting upon potash forms two compounds, the chloride and hypochlorite of potassium (p. 185):

$$ClCl + OKK = ClK + OClK.$$

Again, in the action of chlorine upon many organic compounds, one atom of chlorine removes one atom of hydrogen as hydrochloric acid, while another atom of chlorine takes the place of the hydrogen thus removed. For example, in the formation of chloracetic acid by the action of chorine on acetic acid:

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + ClCl = HCl + \underset{\text{Chloracetic acid.}}{C_2H_3ClO_2}$$

Similarly, when metallic sulphides oxidize in the air, both the metal and the sulphur combine with oxygen; and sulphur acting upon potash forms both a sulphide and a hyposulphite. In all these cases the atoms of the elementary bodies act in pairs.

On the supposition that the molecules of elementary bodies in the gaseous state are made up of two atoms, the specific volumes of these gases will come under the same law as that which applies to compounds (p. 229); and it may then be stated generally, that, with the few exceptions already noticed, *the specific gravities of all bodies, simple and compound, in the gaseous state, are equal to half their molecular weights;* or *the specific volume* (the quotients of the molecular weight by the specific gravities) *are equal to* 2.

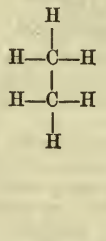
Variation of Equivalency. — Multivalent or polygenic elements often exhibit varying degrees of equivalency. Thus carbon, which is quadrivalent in marsh gas, CH_4, and in carbon dioxide, CO_2, is only bivalent in carbon monoxide, CO; nitrogen, which is quinquivalent in sal-ammoniac, NH_4Cl, and the other ammonium salts, and in nitrogen pentoxide, N_2O_5, is trivalent in ammonia, NH_3, and in nitrogen trioxide, N_2O_3, and univalent in nitrogen monoxide, N_2O; sulphur, also, which is sexvalent in sulphur trioxide, SO_3, is quadrivalent in sulphur dioxide, SO_2, and bivalent in hydrogen sulphide, SH_2, and in many metallic sulphides. In these cases, and in all others of varying equivalency, the variation always takes place by two units of equivalency. It is not very easy to account for these variations; but it is observed in all cases that the compounds in which the equivalency of a polygenic element is most completely satisfied are more stable than the others, and that the latter tend to pass into the former by taking up the required number of univalent or bivalent atoms; thus, carbon monoxide, CO, easily takes up another atom of oxygen to form the dioxide, CO_2; nitrogen trioxide, N_2O_3, is readily converted into the pentoxide, N_2O_5; ammonia, NH_3, unites readily with hydrochloric acid to form sal-ammoniac, NH_4Cl, &c.

Similar phenomena are exhibited by many organo-metallic bodies, as will be explained further on.

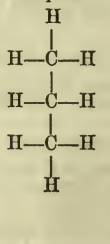
From this it seems most probable that the true equivalency or atomicity of a polygenic element is that which corresponds with the maximum number of monad atoms with which it can combine, but that one or two pairs of its units of equivalency may, under certain circumstances, remain unsaturated. Whether a saturated or an unsaturated element is formed, will depend on a variety of conditions, often in great measure on the relative quantities of the acting substances. Thus, phosphorus, which is a pentad element, forms with chlorine, either a trichloride, PCl_3, or a pentachloride, PCl_5, according as the phosphorus or the chlorine is in excess (p. 217).*

In compounds containing two or more atoms of the same polygenic element, one or more units of equivalence belonging to each of these atoms may be neutralized by combination with those of another atom of the same kind, so that the element in question will appear to enter into the compound with less than its normal degree of equivalence. Thus, in ethane, or dimethyl, C_2H_6, which is a perfectly stable compound, having no tendency to take up an additional number of atoms of hydrogen or any other element, the carbon appears to be trivalent instead of quadrivalent; similarly in propane, C_3H_8, its equivalence appears to be reduced to $\frac{8}{3}$; and in quartane or diethyl, C_4H_{10}, to $\frac{5}{2}$. In all these cases, however, the diminution of equivalent value in the carbon atoms is only apparent, as may be seen from the following formulæ:

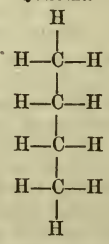
Ethane.



Propane.



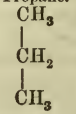
Quartane.



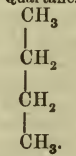
or, more shortly, omitting the equivalent marks of the monad atoms:

Ethane.

Propane.



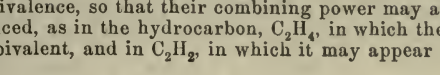
Quartane.



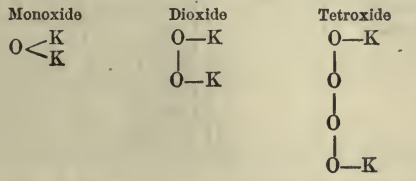
In each of these compounds, every carbon atom, except the two outside ones, has two of its units of equivalence satisfied by combination with those of the neighboring carbon atoms, while each of the two exterior ones has only one unit thus satisfied. Hence in any similarly constituted compound containing n carbon atoms, the number of units of equivalence remaining to be satisfied by the hydrogen atoms is $4n - 2(n-2) - 2 = 2n + 2$. The general formula of this series of hydrocarbons is, therefore, C_nH_{2n+2}, and the equivalent value of the carbon is $\frac{2n+2}{n}$.

* See also Erlenmeyer, "Lehrbuch der organischen Chemie." Leipzig und Heidelberg, 1867, p. 41.

In other cases, multivalent atoms may be united by two or more of their units of equivalence, so that their combining power may appear to be still further reduced, as in the hydrocarbon, C_2H_4, in which the carbon may be apparently bivalent, and in C_2H_2, in which it may appear to be univalent; thus:



In all cases, the equivalent value or atomicity of an element must be determined by the number of monad atoms with which it can combine. Of dyad atoms, indeed, any element or compound may take up an indefinite number, without alteration of its equivalence or combining powers; for each dyad atom, possessing two units of equivalency, neutralizes one unit in the compound which it enters, and introduces another, leaving, therefore, the equivalence or combining power of the compound just what it was before. Thus potassium forms only one chloride, KCl, and is, therefore, univalent or monadic; but in addition to the oxide, K_2O, corresponding to this chloride, it likewise forms two others, viz., K_2O_3 and K_2O_4, in the former of which it might be regarded as dyadic, and in the latter as tetradic; but the manner in which dyad oxygen enters these compounds is easily seen by inspection of the following diagrams:



It is evident that any number of oxygen-atoms might, in like manner, be inserted without disturbing the balance of equivalency. If, indeed, we turn to the sulphides of potassium, in which the sulphur is dyadic, like oxygen, we find the series, K_2S_1, K_2S_2, K_2S_3, K_2S_4, K_2S_5, the constitution of which may be represented in a precisely similar manner. Hence the equivalence of any element must be determined by the composition of its chlorides, bromides, iodides, or fluorides, not by that of its oxides or sulphides.

Assuming then that the maximum equivalence of a polygenic element is that which represents its normal mode of combination, the elementary bodies may be classified as in the following table, in which the names of the metalloïds are printed in italics, those of the metals in Roman type, and the elements are further divided by horizontal lines into groups consisting of elements closely related in their chemical characters: in each of these groups the elements are arranged in the order of their atomic weights, beginning with the lowest. (See Table, p. 226.)

The position of several of the elements in this arrangement must be regarded as still somewhat doubtful. *Nitrogen*, *phosphorus*, *arsenic*, *antimony*, and *bismuth*, though quinquivalent in a considerable number of compounds, as ammonium-chloride, NH_4Cl, phosphorus pentachloride, PCl_5, etc., nevertheless form very stable compounds, as NH_3, $AsCl_3$, As_2O_3, etc., in which they are trivalent. It is true that these compounds pass with tolerable facility into others in which the nitrogen, phosphorus, etc., are quinquivalent, and these latter show no disposition to attach to themselves any additional number of monad atoms; but, on the other hand, these latter

compounds do not appear to be very stable, inasmuch as they easily split up, when volatilized, in such a manner as to yield compounds of the triadic

Monads.	Dyads.	Triads.	Tetrads.	Pentads.	Hexads.
Hydrogen	*Oxygen*	*Boron*	*Carbon*	*Nitrogen*	*Sulphur*
			Silicon	*Phosphorus*	*Selenium*
Fluorine	Calcium	Gold	Titanium	Vanadium	*Tellurium*
Chlorine	Strontium		Tin	Arsenic	
Bromine	Barium	Thallium		Antimony	Chromium
Iodine			Aluminium	Bismuth	Molybdenum
	Berylium		Zirconium		
Lithium	Yttrium			Niobium	Tungsten
Sodium	Lanthanum		Rhodium	Tantalum	
Potassium	Didymium		Ruthenium		
Rubidium	Erbium		Palladium		
Cæsium	Thorinum		Platinum		
			Iridium		
Silver	Magnesium		Osmium		
	Zinc				
	Cadmium		Lead		
	Copper		Manganese		
	Mercury		Iron		
			Cobalt		
			Nickel		
			Cerium		
			Indium		
			Uranium		

class; sal-ammoniac, for example, into hydrochloric acid and ammonia, phosphorus pentachloride into free chlorine and the trichloride:

$$\begin{aligned} NH_4Cl &= HCl + NH_3 \\ PCl_5 &= Cl_2 + PCl_3. \end{aligned}$$

Iron, and the metals which follow it in the table, are sometimes classed as hexads, on account of their analogy with chromium, which is, undoubtedly, hexadic, inasmuch as it forms a hexfluoride, CrF_6. Neither of these metals, however, is known to form any well-defined compounds in which it is more than quadrivalent. Iron, for example, is bivalent in the ferrous salts, as $Fe''Cl_2$, and quadrivalent in the ferric compounds, ferric chloride, Fe_2Cl_6, being constituted in the manner shown by the formula $\left|\begin{matrix} FeCl_3 \\ FeCl_3 \end{matrix}\right.$. Manganese is inferred to be a hexad, on account of the isomorphism and similarity of composition between the magnates and the chromates: but the isomorphism of two elements, or their corresponding compounds, does not afford decided proof of equal equivalency, for the fluoniobates are known to be isomorphous with the fluosilicates and fluotitanates; and yet niobium is a pentad element, whereas silicium and titanium are tetrads.

Sulphur, *selenium*, and *tellurium*, are usually regarded as dyads, on account of the close analogy of their compounds to those of oxygen, and especially of their hydrogen compounds, SH_2, &c., to water. But selenium and tellurium form well-defined tetrachlorides; and even sulphur tetrachloride,

SCl_4, though it has not been obtained in the free state, is known in combination with metallic chlorides. Sulphur has also lately been shown to form certain organic compounds in which it is tetradic, and others in which it appears to be hexadic.* Moreover, the chemical relations of the sulphates are much more clearly represented by formulæ, in which sulphur is supposed to be hexadic (like that given for sulphuric acid on page 231), than by formulæ into which it enters as a dyad; and similar remarks apply to the selenates and tellurates; for these reasons, sulphur, selenium, and tellurium, are most conveniently regarded as hexads, though they sometimes enter into combination as tetrads, and very frequently as dyads.

Compound Radicals. — Suppose one or more of the component atoms of a fully saturated molecule to be removed: it is clear that the remaining atom or group of atoms will no longer be saturated, but will have a combining power corresponding to the number of units of equivalency removed. Such unsaturated groups are called *residues* or *radicals*. Methane, CH_4, is a fully saturated compound; but if one of its hydrogen atoms be removed, the residue CH_3 (called *methyl*), will be ready to combine with one atom of a univalent element, such as chlorine, bromine, &c., forming the compounds CH_3Cl, CH_3Br, &c.; two atoms of it unite in like manner with one atom of oxygen, sulphur, and other bivalent elements, forming the compounds $O''(CH_3)_2$, $S''(CH_3)_2$, &c.; three atoms with nitrogen yielding $N'''(CH_3)_3$, &c.

The removal of two hydrogen-atoms from CH_4 leaves the bivalent radical CH_2, called *methene*, which yields the compounds CH_2Cl_2, CH_2O, CH_2S, &c. The removal of three hydrogen atoms from CH_4 leaves the trivalent radical CH, which, in combination with three chlorine-atoms, constitutes chloroform, $CHCl_3$. And, finally, the removal of all four hydrogen-atoms from CH_4 leaves the quadrivalent radical *carbon* C^{iv}, capable of forming the compounds CCl_4, CS_2, &c.

In like manner, *ammonia*, NH_3, in which the nitrogen is trivalent, yields, by removal of one hydrogen-atom, the univalent radical *amidogen* NH_2, which with one atom of potassium forms potassamine, NH_2K, and when combined with one atom of the univalent radical methyl, CH_3, forms methylamine, $NH_2(CH_3)$, &c. The abstraction of two hydrogen-atoms from the molecule NH_3, leaves the bivalent radical *imidogen*, NH, which with two methyl-atoms forms dimethylamine, $NH(CH_3)_2$, &c.; and the removal of all three hydrogen-atoms from NH_3, leaves *nitrogen* itself, which frequently acts as a trivalent element or radical, forming tripotassamine NK_3, trimethylamine $N(CH_3)_3$, &c.

Finally, the molecule of *water*, OH_2, by losing an atom of hydrogen, is converted into the univalent radical *hydroxyl*, OH, which, in its relations to other bodies, is analogous to chlorine, bromine, and iodine, and may be substituted in combination for one atom of hydrogen or other monads. Thus, water itself may be regarded as H.HO, analogous to hydrochloric acid HCl; potassium hydrate as K.HO, analogous to potassium chloride; barium hydrate, as $Ba''.(OH)_2$, analogous to barium chloride $Ba''Cl_2$.

In a similar manner, the univalent radical, *potassoxyl*, KO, may be derived from potassium hydrate; the bivalent radical, *zincoxyl*, ZnO_2, by abstraction of H_2 from zinc hydrate, $Zn''H_2O_2$. The essential character of these oxygenated radicals is that each of the oxygen atoms contained in them is united to the other atoms by one unit of equivalency only, so that the radical has necessarily one or two units unconnected; thus:

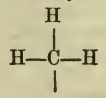
Hydroxyl	H—O—
Potassoxyl	K—O—
Zincoxyl	O—Zn—O—

* Sulphur triethiodide, $S^{iv}(C_2H_5)_3I$
Sulphur diethene-dibromide, $S^{vi}(C_2H_4)''_2Br_2$.

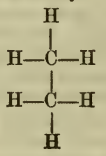
From the preceding explanations of the mode of derivation of compound radicals, it is clear that there is no limit to the number of them which may be supposed to exist; in fact, it is only necessary to suppose a number of units of equivalency abstracted from any saturated molecule, in order to obtain a radical of corresponding combining power or equivalent value. But unless a radical can be supposed to enter into a considerable number of compounds, thus forming them into a group like the salts of the same metal, there is nothing gained in point of simplicity or comprehensiveness by assuming its existence.

It must, also, be distinctly understood that these compound radicals do not necessarily exist in the separate state, and that those of uneven equivalency, like methyl, cannot exist in that state, their molecules, if liberated from combination with others, always doubling themselves, as we have seen to be the case with most of the elementary bodies. Thus hydroxyl —O—H is not known in the free state, the actually existing compound containing the same proportions of hydrogen and oxygen, being O_2H_2 or H—O—O—H. In like manner, methyl, CH_3, has no separate existence, but dimethyl C_2H_6 is a known compound:

Methyl.



Dimethyl.



CHEMICAL AFFINITY.

THE term chemical affinity, or chemical attraction, has been invented to describe that particular power or force, in virtue of which, union, often of a very intimate and permanent nature, takes place between two or more bodies, in such a way as to give rise to a *new* substance, having, for the most part, properties completely in discordance with those of its components.

The attraction thus exerted between different kinds of matter is to be distinguished from other modifications of attractive force which are exerted indiscriminately between all descriptions of substances, sometimes at enormous distances, sometimes at intervals quite inappreciable. Examples of the latter are to be seen in cases of what is called *cohesion*, when the particles of solid bodies are immovably bound together into a mass. Then, there are other effects of, if possible, a still more obscure kind; such as the various actions of surface, the adhesion of certain liquids to glass, the repulsion of others, the ascent of water in narrow tubes, and a multitude of curious phenomena which are described in works on Natural Philosophy, under the head of *molecular actions*. From all these, true chemical attraction may be at once distinguished by the deep and complete change of characters which follows its exertion: we might define affinity to be a force by which new substances are generated.

It seems to be a general law that bodies most opposed to each other in chemical properties evince the greatest tendency to enter into combination; and, conversely, bodies between which strong analogies and resemblances can be traced manifest a much smaller amount of mutual attraction. For example, hydrogen and the metals tend very strongly indeed to combine with oxygen, chlorine, and iodine, but the attraction between the different members of these two groups is incomparably more feeble. Sulphur and phosphorus stand, as it were, midway: they combine with substances of one and the other class, their properties separating them sufficiently from both. Acids are drawn towards alkalies, and alkalies towards acids, while union among themselves rarely if ever takes place.

Nevertheless, chemical combination graduates so imperceptibly into mere mechanical mixture, that it is often impossible to mark the limit. Solution is the result of a weak kind of affinity existing between the substance dissolved and the solvent — an affinity so feeble as completely to lose one of its most prominent features when in a more exalted condition — namely, power of causing elevation of temperature; for in the act of mere solution, the temperature falls, the heat of combination being lost and overpowered by the effects of change of state.

The force of chemical attraction thus varies greatly with the nature of the substances between which it is exerted; it is influenced, moreover, to a very large extent, by external or adventitious circumstances. An idea formerly prevailed that the relations of affinity were fixed and constant between the same substances, and great pains were taken in the preparation of tables exhibiting what was called the precedence of affinities. The order pointed out in these lists is now acknowledged to represent the order of precedence *for the circumstances* under which the experiments were made, but nothing more; so soon as these circumstances become changed, the order is disturbed. The ultimate effect, indeed, is not the result of the exercise of one single force, but rather the joint effect of a number, so complicated and so variable in intensity, that it is but seldom possible to predict the consequences of any yet untried experiment.

It will be proper to examine shortly some of these extraneous causes to

which allusion has been made, which modify to so great an extent the direct and original effects of the specific attractive force.

Alteration of temperature may be reckoned among these. When metallic mercury is heated nearly to its boiling-point, and in that state exposed for a lengthened period to the air, it absorbs oxygen, and becomes converted into a dark-red crystalline powder. This very same substance, when raised to a still higher temperature, separates spontaneously into metallic mercury and oxygen gas. It may be said, and probably with truth, that the latter change is greatly aided by the tendency of the metal to assume the vaporous state; but precisely the same fact is observed with another metal, palladium, which is not volatile, excepting at extremely high temperatures, but which oxidizes superficially at a red heat, and again becomes reduced when the temperature rises to whiteness.

Insolubility and the power of vaporization are perhaps, beyond all other disturbing causes, the most potent; they interfere in almost every reaction which takes place, and very frequently turn the scale when the opposed forces do not greatly differ in energy. It is easy to give examples. When a solution of calcium chloride is mixed with a solution of ammonium carbonate, double interchange ensues, calcium carbonate and ammonium chloride being generated: $-CaCl_2 + CO_3\ (NH_4)_2 = CO_3Ca + 2NH_4Cl$. Here the action can be shown to be in a great measure determined by the insolubility of the calcium carbonate. Again, when dry calcium carbonate is powdered and mixed with ammonium chloride, and the whole heated in a retort, a sublimate of ammonium carbonate is formed, while calcium chloride remains behind. In this instance, it is no doubt the great volatility of the new ammoniacal salt which chiefly determines the kind of decomposition.

When iron filings are heated to redness in a porcelain tube, and vapor of water passed over them, the water undergoes decomposition with the utmost facility, hydrogen being rapidly disengaged, and the iron converted into oxide. On the other hand, oxide of iron, heated in a tube through which a stream of dry hydrogen is passed, suffers almost instantaneous reduction to the metallic state, while the vapor of water, carried forward by the current of gas, escapes as a jet of steam from the extremity of the tube. In these experiments the affinities between the iron and oxygen and the hydrogen and oxygen are so nearly balanced, that the difference of *atmosphere* is sufficient to settle the point. An atmosphere of steam offers little resistance to the escape of hydrogen; an atmosphere of hydrogen bears the same relation to steam; and this apparently trifling difference of circumstances is quite enough for the purpose.

The decomposition of vapor of water by white-hot platinum, pointed out by Mr. Grove, will probably be referred in great part to this influence of atmosphere, the steam offering great facilities for the assumption of the elastic condition by the oxygen and hydrogen. The decomposition ceases as soon as these gases amount to about $\frac{1}{3000}$ of the bulk of the mixture, and can only be renewed by their withdrawal. The attraction of oxygen for hydrogen is probably much weakened by the very high temperature. The recombination of the gases by the heated metal is rendered impossible by their state of dilution.

What is called the nascent state is one very favorable to chemical combination. Thus, nitrogen refuses to combine with gaseous hydrogen; yet when these substances are simultaneously liberated from some previous combination, they unite with great ease, as when organic matters are destroyed by heat, or by spontaneous putrefactive change.

There is a remarkable, and, at the same time, very extensive class of actions, grouped together under the general title of cases of *disposing affinity*. Metallic silver does not oxidize at any temperature: nay, more, its oxide is easily decomposed by simple heat; yet if the finely divided metal be mixed with siliceous matter and alkali, and ignited, the whole

fuses to a yellow transparent glass of silver silicate. Platinum is attacked by fused potassium hydrate, hydrogen being probably disengaged while the metal is oxidized: this is an effect which never happens to silver under the same circumstances, although silver is a much more oxidable substance than platinum. The fact is, that potash forms with the oxide of the last-named metal a kind of saline compound, in which the platinum oxide acts as an acid; and hence its formation under the *disposing* influence of the powerful base.

In the remarkable decompositions suffered by various organic bodies when heated in contact with caustic alkali or lime, we have other examples of the same fact. Products are generated which are never formed in the absence of the base; the reaction is invariably less complicated, and its results few in number and more definite, than in the event of simple destruction by a graduated heat.

There is yet a still more obscure class of phenomena, called *catalysis*, in which effects are brought about by the mere *presence* of a substance which itself undergoes no perceptible change: the experiment mentioned in the chapter on oxygen, in which that gas is obtained, with the greatest facility, by heating a mixture of potassium chlorate and manganese dioxide, is an excellent case in point. The salt is decomposed at a very far lower temperature than would otherwise be required, and yet the manganese oxide does not appear to undergo any alteration, being found after the experiment in the same state as before. It may, however, undergo a temporary alteration. We know, indeed, that this oxide is capable of taking up an additional proportion of oxygen and forming manganic acid; and it is quite possible that in the reaction just considered it may actually take oxygen from the potassium chlorate, and pass to the state of a higher oxide, which, however, is immediately decomposed, the additional oxygen being evolved, and the manganese-oxide returning to its original state. The same effect in facilitating the decomposition of the chlorate is produced by cupric oxide, ferric oxide, and lead oxide, all of which are known to be susceptible of higher oxidation. The oxides of zinc and magnesium, on the contrary, which do not form higher oxides, are not found to facilitate the decomposition of the chlorate; neither is any such effect produced by mixing the salt with other pulverulent substances, such as pounded glass or pure silica.

The so-called catalytic actions are often mixed up with other effects which are much more intelligible, as the action of finely divided platinum on certain gaseous mixtures, in which the solid appears to condense the gas upon its greatly extended surface, and thereby to induce combination by bringing the particles within the sphere of their mutual attractions.

Relations of Heat to Chemical Affinity. — Whatever may be the real nature of chemical affinity, one most important fact is clearly established with regard to it; namely, that its manifestations are always accompanied by the production or annihilation of heat. Change of composition, or chemical action, and heat are mutually convertible: a given amount of chemical action will give rise to a certain definite amount of heat, which quantity of heat must be directly or indirectly expended, in order to reverse or undo the chemical action that has produced it. The production of heat by chemical action, and the definite quantitative relation between the amount of heat evolved and the quantity of chemical action which takes place, are roughly indicated by the facts of our most familiar experience; thus, for instance, the only practically important method of producing heat artificially consists in changing the elements of wood and coal, together with atmospheric oxygen, into carbon dioxide and water; and every one knows that the heat which can be thus obtained from a given quantity of coal is limited, and is, at least approximately, always the same.

The accurate measurement of the quantity of heat produced by a given amount of chemical action is a problem of very great difficulty; chiefly because chemical changes very seldom take place alone, but are almost always accompanied by physical changes involving further calorimetric effects, each of which requires to be accurately measured and allowed for, before the effect due to the chemical action can be rightly estimated. Thus the ultimate result has, in most cases, to be deduced from a great number of independent measurements, each of which is liable to a certain amount of error. It is therefore not surprising that the results of various experiments should differ to a comparatively great extent, and that some uncertainty should still exist as to the exact quantity of heat corresponding to even the simplest cases of chemical action.

The experiments are made by enclosing the acting substances in a vessel called a calorimeter, surrounded by water or mercury, the rise of temperature in which indicates the quantity of heat evolved by the chemical action, after the necessary corrections have been made for the heat absorbed by the containing vessel and the other parts of the apparatus, and for the amount lost by radiation, &c. Combustions in oxygen and chlorine are made in a copper vessel surrounded by water; the heat evolved by the mutual action of liquids or dissolved substances is estimated by means of a smaller calorimeter containing mercury. The construction of these instruments and the methods of observation involve details which are beyond the limits of this work.*

The following table gives the quantities of heat, expressed in heat-units,† evolved in the combustion of various elements, and a few compounds, in oxygen, referred: (1) to 1 gram of each substance burned; (2) to 1 gram of oxygen consumed; (3) to one atom or molecule (expressed in grams) of the various substances: —

Heat of Combustion of Elementary Substances in Oxygen.

Substance.	Product.	Units of heat evolved			Observer.
		by 1 grm. of substance.	by 1 gram of oxygen.	by 1 at. of substance.	
Hydrogen . . .	OH_2	33881	4235	53881	Andrews.
		34462	4308	64462	Favre & Silbermann.
Carbon:					
Wood-charcoal	CO_2	7900	2962	94800	Andrews.
		8080	3030	96960	Favre & Silbermann.
Gas retort carbon	"	8047	3018	96564	" "
Native graphite	"	7797	2924	93564	" "
Artificial graphite	"	7762	2911	93144	" "
Diamond . . .	"	7770	2914	93940	" "
Sulphur:					
Native	SO_2	2220	2220	71040	" "
Recently melted .	"	2260	2260	72320	" "
Flowers . . .	"	2307	2307	73821	Andrews.
Phosphorus:					
(Yellow) . . .	P_2O_5	5747	4454	178157	"
Zinc	ZnO	1330	5390	86450	"
Iron	Fe_3O_4	1582	4153	88592	"
Tin	SnO_2	1147	4230	135360	"
Copper	CuO	603	2394	38304	"

* See Miller's Chemical Physics, pp. 338, *et seq.*, and Watts's Dictionary of Chemistry, iii. 28, 103.

† The unit of heat here adopted, is the quantity of heat required to raise 1 gram of water from 0° to 1° C.

The following results have been obtained by the complete combustion of partially oxidized substances:

Substance.	Product.	Units of heat evolved		Observer.
		by 1 grm. of substance.	in formation of 1 molecule of the ultimate product.	
Carbon monoxide, CO	CO_2	2403	67284	Favre & Silbermann.
		2431	68064	Andrews.
Stannous oxide, SnO	SnO_2	519	69584	"
Cuprous oxide, Cu_2O	CuO	256	18304	"

The last three substances in this table contain exactly half as much oxygen as the completely oxidized products; and on comparing the amount of heat evolved in the formation of one molecule of stannic or cupric oxide from the corresponding lower oxide, with the quantity produced when a molecule of the same product is formed by the complete oxidation of the metal in one operation, we find that the combination of the second half of the oxygen contained in these bodies evolves sensibly half as much as the combination of the whole quantity. In the formation of carbon dioxide, however, the second half of the oxygen appears to develop more than two thirds of the total amount of heat; but this result is probably due, in part at least, to the fact that when carbon is burned into carbon dioxide, a considerable but unknown quantity of heat is expended in converting the solid carbon into gas, and thus escape measurement; while, in carbon monoxide, the carbon already exists in the gaseous form, and therefore no portion of the heat evolved in the combustion of this substance is similarly expended in producing a change of state.

It seems probable, also, that a similar explanation may be given of the inequalities in the quantities of heat produced by the combustion of different varieties of pure carbon and of sulphur — that is to say, that a portion of the heat generated by the combustion of diamond and graphite goes to assimilate their molecular condition to that of wood-charcoal, and that there is an analogous expenditure of heat in the combustion of native sulphur.

Combustions in Chlorine, and Direct Combination of Chlorine, Bromine, and Iodine with other Elements. — The following table gives the quantities of heat evolved by the direct union of various elements with gaseous chlorine:

Substance.	Product.	Units of heat evolved			Observer.
		by 1 gram of substance.	by 1 grm. of chlorine.	by 1 at. (= 35·5 grams) of chlorine.	
Hydrogen	HCl	24087	678	24087	Abria.
		23783	670	23783	Favre & Silbermann.
Phosphorus	PCl_5 (?)	3422 (?)	607	21548	Andrews.
Potassium	KCl	2655	2943	104476	"
Iron	Fe_2Cl_6	1745	921	32695	"
Zinc	$ZnCl_2$	1529	1427	50658	"
Tin	$SnCl_4$	1079	897	31722	"
Arsenic	$AsCl_3$	994	704	24992	"
Copper	$CuCl_2$	961	859	30494	"
Antimony	$SbCl_3$	707	860	30491	"
Mercury	?	?	822	29181	"

The heat evolved by the direct union of bromine and iodine with zinc and iron has also been determined by Andrews: the results obtained are given in the next table:

Metal.	Product.	Units of heat evolved		
		by 1 gram of metal.	by 1 gram of bromine or iodine.	by 1 atom of bromine or iodine.
Bromine.				
Zinc . .	$ZnBr_2$	1269	508	40640
Iron . .	Fe_2Br_6	1277	298	23833
Iodine.				
Zinc . .	ZnI_2	819	209	26617
Iron . .	Fe_2I_6	463	63	8046

Reactions in Presence of Water. — The thermal effects which may result from the reaction of different substances on one another in presence of water, are more complicated than those resulting from direct combination. In addition to the different specific heats of the reagents and products, and to the different quantities of heat absorbed by them in dissolving, or given out by them in combining with water, the conversion of soluble substances into insoluble ones, as a consequence of the chemical action, or the inverse change of insoluble into soluble bodies, are among the secondary causes to which part of the calorimetric effect may be due in these cases.

When a gas dissolves in water, the heat due to the chemical action is augmented by that due to the liquefaction of the gas; so also when a solid body is dissolved in water, the total thermal effect is due in part to the chemical action taking place between the water and the solid, and in part to the liquefaction of the substance dissolved. In the former cases the chemical and physical parts of the phenomenon both cause evolution of heat; in the latter case the physical change occasions disappearance of heat, and if this effect is greater than that due to the chemical action, the ultimate effect is the production of cold, and it is this which is generally observed.

Cold produced by Chemical Decomposition. — It is highly probable that the thermal effect of the reversal of a given chemical action is in all cases equal and opposite to the thermal effect of that action itself. A direct consequence of this proposition is that *the separation of any two bodies is attended with the absorption of a quantity of heat equal to that which is evolved in their combination.* The truth of this deduction has been experimentally established in various cases, by Wood,* Joule,† and Favre and Silbermann, by comparing the heat evolved in the electrolysis of dilute sulphuric acid, or solutions of metallic salts, with that which is developed in a thin metallic wire by a current of the same strength; also by comparison of the heat evolved in processes of combination accompanied by simultaneous decomposition, with that evolved when the same combination occurs between free elements.

By determining the heat evolved when different metals were dissolved in water or dilute acid, Wood found that it was less than that which would be produced by the direct oxidation of the same metals, by a quantity equal to that which would be obtained by burning the hydrogen set free, or which was expended in decomposing the water or acid: and, therefore, that when this latter quantity was added to the results, they agreed with the numbers given by experiments of direct oxidation.

* Phil. Mag. [4] ii. 368; iv. 370. † *Ibid.* iii. 481.

ELECTRO-CHEMICAL DECOMPOSITION; CHEMISTRY OF THE VOLTAIC PILE.

When a voltaic current of considerable power is made to traverse various compound liquids, a separation of the elements of these liquids ensues; provided that the liquid be capable of conducting the current, its decomposition almost always follows.

The elements are disengaged solely at the limiting surfaces of the liquid, where, according to the common mode of speech, the current enters and leaves the latter, all the intermediate portions appearing perfectly quiescent. In addition, the elements are not separated indifferently and at random at these two surfaces; but, on the contrary, make their appearance with perfect uniformity and constancy at one or the other, according to their chemical character — namely, oxygen, chlorine, iodine, acids, &c., at the surface connected with the *copper*, or *positive* end of the battery; hydrogen, the metals, &c., at the surface in connection with the *zinc* or *negative* extremity of the arrangement.

The terminations of the battery itself — usually, but by no means necessarily, of metal — are designated poles or *electrodes*,* as by their intervention the liquid to be experimented on is made a part of the circuit. The process of decomposition by the current is called *electrolysis*,† and the liquids, which, when thus treated, yield up their elements, are denominated *electrolytes*.

When a pair of platinum plates are plunged into a glass of water to which a few drops of oil of vitriol have been added, and the plates connected by wires with the extremities of an active battery, oxygen is disengaged at the positive electrode, and hydrogen at the negative, in the proportion of one measure of the former to two of the latter nearly. This experiment has before been described.‡

A solution of hydrochloric acid mixed with a little Saxon blue (indigo), and treated in the same manner, yields hydrogen on the negative side and chlorine on the positive, the indigo there becoming bleached.

Potassium iodide dissolved in water is decomposed in a similar manner: the free iodine at the positive side can be recognized by its brown color, or by the addition of a little gelatinous starch.

All liquids are not electrolytes; many refuse to conduct, and no decomposition can then occur; alcohol, ether, numerous essential oils, and other products of organic chemistry, besides a few saline inorganic compounds, act in this manner, and completely arrest the current of a powerful battery.

One of the most important and indispensable conditions of electrolysis is fluidity: bodies which, when reduced to the liquid state, conduct freely, and as freely suffer decomposition, become absolute insulators to the electricity of the battery when they become solid. Lead chloride offers a good illustration of this fact: when fused in a porcelain crucible, it gives up its elements with the utmost ease, and a galvanometer, interposed somewhere in the circuit, is strongly affected. But when the source of heat is withdrawn, and the salt suffered to solidify, signs of decomposition cease, and at the same moment the magnetic needle reassumes its natural position. In the same manner, the thinnest film of ice arrests the current

* From ἤλεκτρον, and ὁδός, a way.

† From ἤλεκτρον, and λύειν, to loose.

‡ Page 143.

of a powerful voltaic apparatus; but the instant the ice is liquefied at any one point, so that water communication is restored between the electrodes, the current again passes, and decomposition occurs. Fusion by heat, and solution in aqueous liquids, answer the purpose equally well.

Generally speaking, compound liquids cannot conduct the electric current without being decomposed; but still there are a few exceptions to this statement, which perhaps are more apparent than real. Thus Hittorf has shown, that fused silver sulphide, which was formerly regarded as one of the exceptions, cannot be considered to be so, and Beetz has since proved the same to be the case as regards mercuric iodide and lead fluoride.

The quantity of any given compound liquid which can be decomposed by any given electric battery depends on the resistance of the liquid: the more resistance the less decomposition. Distilled water has only a small power of conduction, and is therefore only slightly decomposed by a battery of 30 to 40 pairs; whilst diluted sulphuric acid is one of the best of fluid conductors, and undergoes rapid decomposition by a small battery.

When a liquid which can be decomposed, and a galvanometer, are included in the circuit of an electric current, if the needle of the galvanometer be deflected, it may be always assumed as certain that a portion of liquid, bearing a proportion to the strength of the current, is decomposed, although it may be impossible in many cases, without special contrivances, to detect the products of the decomposition, on account of their minuteness.

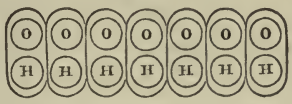
The metallic terminations of the battery, the poles or electrodes, have, in themselves, nothing in the shape of attractive or repulsive power for the elements separated at their surfaces. Finely divided metal suspended in water, or chlorine held in solution in that liquid, shows not the least symptom of a tendency to accumulate around them; a single element is altogether unaffected — directly, at least; separation from previous combination is required, in order that this appearance should be exhibited.

It is necessary to examine the process of electrolysis a little more closely. When a portion of hydrochloric acid, for example, is subjected to decomposition in a glass vessel with parallel sides, chlorine is disengaged at the positive electrode, and hydrogen at the negative: the gases are perfectly pure and unmixed. If, while the decomposition is rapidly proceeding, the intervening liquid be examined by a beam of light, or by other means, not the slightest disturbance or movement of any kind will be perceived; nothing like currents in the liquid or bodily transfer of gas from one part to another can be detected; and yet two portions of hydrochloric acid, separated perhaps by an interval of four or five inches, may be respectively evolving pure chlorine and pure hydrogen.

There is, it would seem, but one mode of explaining this and all similar cases of regular electrolitic decomposition: this is by assuming that *all* the particles of hydrochloric acid between the electrodes, and by which the current is conveyed, simultaneously suffer decomposition, the hydrogen travelling in one direction, and the chlorine in the other. The neighboring elements, thus brought into close proximity, unite and reproduce hydrochloric acid, again destined to be decomposed by a repetition of the same change. In this manner, each particle of hydrogen may be made to travel in one direction, by becoming successively united to each particle of chlorine between itself and the negative electrode; when it reaches the latter, finding no disengaged particle of chlorine for its reception, it is rejected, as it were, from the series, and thrown off in a separate state. The same thing happens to each particle of chlorine, which at the same time passes continually in the opposite direction, by combining successively with each particle of hydrogen that moment separated, with which it meets, until at length it arrives at the positive plate or wire, and is disengaged. A suc-

cession of particles of hydrogen are thus continually thrown off from the decomposing mass at one extremity, and a corresponding succession of particles of chlorine at the other. The power of the current is exerted with equal energy in every part of the liquid conductor, though its *effects* become manifest only at the very extremities. The action is one of a purely molecular or internal nature, and the metallic terminations of the battery merely serve the purpose of completing the connection between the latter and the liquid to be decomposed. The figures 141 and 142 are

Fig. 141.

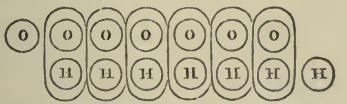


Hydrochloric acid in its usual state.

intended to assist the imagination of the reader, who must at the same time avoid regarding them in any other light than that of a somewhat figurative mode of representing the curious phenomena described. The circles are intended to indicate the elements, and are distinguished by their respective symbols.

Like hydrochloric acid, all electrolytes, when acted on by electricity, are split into two constituents, which pass in opposite directions. The one

Fig. 142.



Hydrochloric acid undergoing electrolysis.

class of substances, like oxygen, chlorine, &c., are evolved at the positive electrode; the other class, like hydrogen and the metals, at the negative electrode.

It is of importance to remark that oxygen salts, such as sulphates and nitrates, when acted on by the current, do not divide into acid and basic oxide, but, as Daniell and Miller proved, into metal and a compound substance, or group of elements, which is transferred in such a state of association that, as regards its electrical behavior, it represents an element. Thus, cupric sulphate, SO_4Cu, splits, not into SO_3 and CuO, but into metallic copper and *sulphione* SO_4. Hydrogen sulphate, or sulphuric acid, SO_4H_2, divides into the same compound group and hydrogen. In a similar way, also, the part of the electrolyte which passes to the negative pole may consist of a group of elements. A solution of sal-ammoniac, NH_4Cl, furnishes a beautiful instance of this fact, since it is decomposed by the current in such a manner that the ammonium NH_4 goes to the negative, and the chlorine to the positive pole.

A distinction must be carefully drawn between true and regular electrolysis, and what is called secondary decomposition, brought about by the reaction of the bodies so eliminated upon the surrounding liquid, or upon the substance of the electrodes: hence the advantage of platinum for the latter purpose, when electrolytic actions are to be studied in their greatest simplicity, that metal being scarcely attacked by any ordinary agents. When, for example, a solution of lead nitrate or acetate is decomposed by

the current between platinum plates, metallic lead is deposited at the negative side, and a brown powder, lead dioxide, at the positive: the latter substance is the result of a secondary action; it proceeds, in fact, from the nascent oxygen at the moment of its liberation reacting upon the monoxide of lead present in the salt, and converting it into dioxide, which is insoluble in the dilute acid. When nitric acid is decomposed, no hydrogen appears at the negative electrode, because it is oxidized at the expense of the acid, which is reduced to nitrous acid gas. When potassium sulphate, SO_4K_2, is electrolyzed, hydrogen appears at the negative electrode, together with an equivalent quantity of potassium hydrate OKH, because the potassium which is evolved at the electrode immediately decomposes the water there present. At the same time, the sulphione, SO_4, which is transferred to the positive electrode, takes hydrogen from the water there present, forming sulphuric acid, SO_4H_2, and liberating oxygen. In like manner hydrogen sulphate, or sulphuric acid itself, is resolved by the current into hydrogen and sulphione, which latter decomposes the water at the positive electrode, reproducing hydrogen sulphate, and liberating oxygen, just as if the water itself were directly decomposed by the current into hydrogen and oxygen. A similar action takes place in the electrolytic decomposition of any other oxygen-salt of an alkali-metal, or alkaline earth-metal, alkali and hydrogen gas making their appearance at the negative electrode, acid and oxygen gas at the positive electrode. This observation explains a circumstance which much perplexed the earlier experimenters upon the chemical action of the voltaic battery. In all experiments in which water was decomposed, both acid and alkali were liberated at the electrodes, even though distilled water was employed; and hence it was believed for some time that the voltaic current had some mysterious power of generating acid and alkaline matter. The true source of these compounds was, however, traced by Davy,* who showed that they proceeded from impurities either in the water itself, or in the vessels which contained it, or in the surrounding atmosphere. Having proved that ordinary distilled water always contains traces of saline matter, he redistilled it at a temperature below the boiling-point, in order to avoid all risk of carrying over salts by splashing. He then found that when marble cups were used to contain the water used for decomposition, hydrochloric acid appeared at the positive electrode, soda at the negative, both being derived from sodium-chloride present in the marble; when agate cups were used, he obtained silica; and when he used gold vessels, he obtained nitric acid and ammonia, which he traced to atmospheric air. By operating in a vacuum, indeed, the quantity of acid and alkali was reduced to a minimum, but the decomposition was almost arrested, although he operated with a battery of fifty pairs of 4-inch plates. Hence it is manifest that *water itself is not an electrolyte*, but that it is enabled to convey the current if it contains only traces of saline matter.†

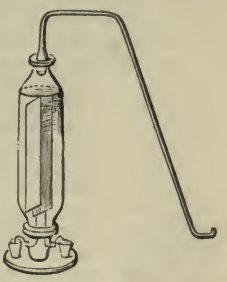
If a number of different electrolytes, such as dilute sulphuric acid, cupric sulphate, potassium iodide, fused lead chloride, &c., be arranged in a series, and the same current be made to traverse the whole, all will suffer decomposition at the same time, but by no means to the same amount. If arrangements be made by which the quantities of the eliminated elements can be accurately ascertained, it will be found, when the decomposition has proceeded to some extent, that these latter have been disengaged exactly in the *ratio of their chemical equivalents*. The same current which decomposes 9 parts of water will separate into their elements 166 parts of potassium iodide, 139 parts of lead chloride, &c. Hence the very important conclusion: *The action of the current is perfectly definite in its nature, producing a fixed and constant amount of decomposition, expressed in each electrolyte by the value of its chemical equivalent.*

* Philosophical Transactions, 1807.

† Miller's Chemical Physics, p. 484.

From a very extended series of experiments, based on this and other methods of research, Faraday was enabled to draw the general inference that effects of chemical decomposition are always proportionate to the quantity of circulating electricity, and may be taken as an accurate and trustworthy measure of the latter. Guided by this highly important principle, he constructed his *voltameter*, an instrument which has rendered the greatest service to electrical science. This is merely an arrangement by which dilute sulphuric acid is decomposed by the current, the gas evolved being collected and measured. By placing such an instrument in any part of the circuit, the quantity of electric force necessary to produce any given effect can be at once estimated; or, on the other hand, any required amount of the latter can be, as it were, measured out and adjusted to the object in view. The voltameter has received many different forms: one of the most extensively useful is that shown in fig. 143, in which the platinum plates are separated by a very small interval, and the gas is collected in a graduated jar standing on the shelf of the pneumatic trough, the tube of the instrument, which is filled to the neck with dilute sulphuric acid, being passed beneath the jar.

Fig. 143.



The decompositions produced by the voltaic battery can be effected by the electricity of the common machine, by that developed by magnetic action, and by that of animal origin, but to an extent incomparably more minute. This arises from the very small *quantity* of electricity set in motion by the machine, although its *tension* — that is, power of overcoming obstacles, and passing through imperfect conductors — is exceedingly great. A pair of small wires of zinc and platinum, dipping into a single drop of dilute acid, develop far more electricity, to judge from the chemical effects of such an arrangement, than very many turns of a large plate electrical machine in powerful action. Nevertheless, polar or electrolytic decomposition can be distinctly and satisfactorily effected by the latter, although on a minute scale.

With a knowledge of the principles laid down, the study of the voltaic battery may be resumed and completed. In the first place, two very different views have been held concerning the source of the electrical disturbance in that apparatus. Volta himself ascribed it to mere contact of dissimilar metals or other substances conducting electricity, — to what was denominated an *electro-motive* force, called into being by such contact. Proof was supposed to be given of this fundamental proposition by an experiment in which discs of zinc and copper attached to insulating handles, after being brought into close contact, were found, by the aid of a very delicate gold-leaf electroscope, to be in opposite electrical states. It appears, however, that the more carefully this experiment is made, the smaller is the effect observed; and hence it is judged highly probable that the whole may be due to accidental causes, against which it is almost impossible to guard.

On the other hand, the observation was soon made that the power of the battery always bears some kind of proportion to the chemical action upon the zinc; that, for instance, when pure water is used, the effect is extremely feeble; with a solution of salt, it becomes much greater; and, lastly, with dilute acid, greatest of all; so that some relation evidently exists between the chemical effect upon the metal and the evolution of electrical force.

The experiments of Faraday and Daniell have given very great support to the chemical theory, by showing that the contact of dissimilar metals is *not* necessary in order to call into being powerful electrical currents, and

that the development of electrical force is not only in some way connected with the chemical action of the liquid of the battery, but that it is always in direct proportion to the latter. One very beautiful experiment, in which electrolytic decomposition of potassium iodide is performed by a current generated without any contact of dissimilar metals, can be thus made: A plate of zinc is bent at a right angle, and cleaned by rubbing with sand-paper. A plate of platinum has a wire of the same metal attached to it by careful riveting, and the latter bent into an arch. A piece of folded filter-paper is wetted with solution of potassium iodide, and placed upon the zinc; the platinum plate is arranged opposite to the latter, with the end of its wire resting upon the paper; and then the pair is plunged into a glass of dilute sulphuric, mixed with a few drops of nitric acid. A brown spot of iodine becomes in a moment evident beneath the extremity of the platinum wire — that is, at the positive side of the arrangement.

Fig. 144.

A strong argument in favor of the chemical view is founded on the easily proved fact, that the direction of the current is determined by the kind of action upon the metals, the one least attacked being always positive. Let two polished plates, the one iron and the other copper, be connected by wires with a galvanometer, and then immersed in a solution of an alkaline sulphide. The needle in a moment indicates a powerful current, passing from the copper through the liquid to the iron, and back again through the wire. Let the plates be now removed, cleaned, and plunged into dilute acid; the needle is again driven round, but in the opposite direction, the current now passing from the iron through the liquid to the copper. In the first instance, the copper is acted upon, and not the iron; in the second, these conditions are reversed, and with them the direction of the current.

The metals employed in the practical construction of voltaic batteries are zinc for the active metal, and copper, silver, or, still better, platinum, for the inactive one: the greater the difference of oxidability, the better the arrangement. The liquid is either dilute sulphuric acid, sometimes mixed with a little nitric, or occasionally, where very slow and long-continued action is wanted, salt and water. To obtain the maximum effect of the apparatus with the least expenditure of zinc, that metal must be employed in a pure state, or its surface must be covered by an amalgam, which in its electrical relations closely resembles the pure metal. The zinc is easily brought into this condition by wetting it with dilute sulphuric acid, and then rubbing a little mercury over it, by means of a piece of rag tied to a stick.

The principle of the compound battery is, perhaps, best seen in the crown of cups: by each alternation of zinc, fluid, and copper, the current is urged forward with increased energy; its intensity is augmented, but the actual amount of electrical force thrown into the current form is not increased. The quantity, estimated by its decomposing power, is, in fact, determined by that of the smallest and least active pair of plates, the quantity of electricity in every part or section of the circuit being exactly equal. Hence large and small plates, batteries strongly and weakly charged, can never be connected without great loss of power.

When a battery, either simple or compound, constructed with pure or with amalgamated zinc, is charged with dilute sulphuric acid, a number of highly interesting phenomena may be observed. While the circuit remains broken, the zinc is perfectly inactive, no acid is decomposed, no hydrogen liberated; but the moment the connection is completed, torrents of hydrogen arise, not from the zinc, but from the copper or platinum surfaces alone,

while the zinc undergoes tranquil and imperceptible oxidation and solution. Thus, exactly the same effects are seen to occur in every active cell of a closed circuit, that are witnessed in a portion of sulphuric acid undergoing electrolysis: oxygen appears at the positive side, with respect to the current, and hydrogen at the negative; but with this difference: that the oxygen, instead of being set free, combines with the zinc. It is, in fact, a real case of electrolysis, and electrolytes alone are available as exciting liquids.

Common zinc is very readily attacked and dissolved by dilute sulphuric acid; and this is usually supposed to arise from the formation of a multitude of little voltaic circles, by the aid of particles of foreign metals or graphite, partially imbedded in the zinc. This gives rise in the battery to what is called local action, by which, in the common forms of apparatus, three fourths or more of the metal are often consumed, without contributing in the least to the general effect, but, on the contrary, injuring it to some extent. This evil is got rid of by amalgamating the surface.

From experiments very carefully made with a "dissected" battery of peculiar construction, in which local action was completely avoided, it has been distinctly proved that the quantity of electricity set in motion by the battery varies exactly with the zinc dissolved. Coupling this fact with that of the definite action of the current, it will be seen that when a perfect battery of this kind is employed to decompose hydrochloric acid, in order to evolve 1 grain of hydrogen from the latter, 32·5 grains of zinc must be dissolved as chloride, and its equivalent quantity of hydrogen disengaged in each active cell of the battery — that is to say, that the electrical force generated by the solution of an equivalent of zinc *in* the battery is capable of effecting the decomposition of an equivalent of hydrochloric acid or any other electrolyte *out* of it.

This is an exceedingly important discovery: it serves to show, in the most striking manner, the intimate nature of the connection between chemical and electrical forces, and their remarkable quantitative or equivalent relations. It almost seems, to use an expression of Faraday, as if a transfer of chemical force took place through the substance of solid metallic conductors; that chemical actions, called into play in one portion of the circuit, could be made at pleasure to exhibit their effects without loss or diminution in any other.

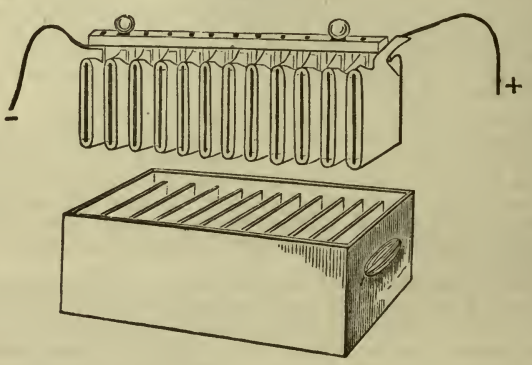
There is an hypothesis, not of recent date, long countenanced and supported by the illustrious Berzelius, which refers all chemical phenomena to electrical forces — which supposes that bodies combine because they are in opposite electrical states; even the heat and light accompanying chemical union may be, to a certain extent, accounted for in this manner. In short, we are in such a position, that either may be assumed as cause or effect: it may be that electricity is merely a form or modification of ordinary chemical affinity; or, on the other hand, that all chemical action is a manifestation of electrical force.

This electro-chemical theory is no longer received as a true explanation of chemical phenomena to the full extent intended by its author. Berzelius, indeed, supposed that the combining tendencies of elements, and their functions in compounds, depend altogether on their electric polarity; and accordingly he divided the elements into two classes, the *electro-positive*, which, like hydrogen and the metals, move towards the negative pole of the battery, as if they were attracted by it, and the *electro-negative*, which, like oxygen, chlorine, and bromine, move towards the positive pole. We are, however, acquainted with a host of phenomena which show that the chemical functions of an element depend upon its position with regard to other elements in a compound, quite as much as upon its individual character. Thus chlorine, the very type of an electro-negative element, can be substituted for hydrogen, one of the most positive of the elements, in a large

number of compounds, yielding new products, which exhibit the closest analogy in composition and properties to the compounds from which they are derived. It is impossible, therefore, to admit that the chemical functions of bodies are determined exclusively by their electrical relations. Still it is true in a general way that those elements which differ most strongly in their electrical characters, chlorine and potassium, for example, are likewise those which combine together with the greatest energy; and the division of bodies into electro-positive and electro-negative is therefore retained; the former are also called *acid* or *chlorous*, and the latter *basylous* or *zincous*.

One of the most useful forms of the common voltaic battery is that contrived by Dr. Wollaston (fig. 145). The copper is made completely to encircle the zinc plate, except at the edges, the two metals being kept apart by pieces of cork or wood. Each zinc is soldered to the preceding copper, and the whole screwed to a bar of dry mahogany, so that the plates can be lifted into or out of the acid, which is contained in an earthenware trough, divided into separate cells. The liquid consists of a mixture of 100 parts water, $2\frac{1}{4}$ parts oil of vitriol, and 2 parts commercial nitric acid, all by measure. A number of such batteries are easily connected together by straps of sheet copper, and admit of being put into action with great ease.

Fig. 145.

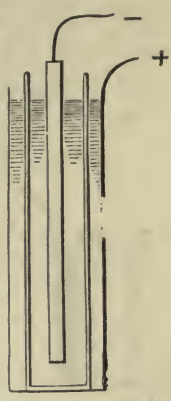


The great objection to this and to all the older forms of the voltaic battery is, that the power rapidly decreases, so that, after a short time, scarcely the tenth part of the original action remains. This loss of power depends, partly on the gradual change of the sulphuric acid into zinc sulphate, but still more on the coating of hydrogen, and, at a later stage, on the precipitation of metallic zinc on the copper plates. It is self-evident that if the copper plate in the liquid became covered with zinc, it would act electrically like a zinc plate. This is precisely the action of the hydrogen, whereby a decrease of electrical power is produced. This effect, produced by the substances separated from the liquid, is commonly called polarization.

An apparatus of immense value for purposes of electro-chemical research, in which it is desired to maintain powerful and equable currents for many successive hours, has been contrived by Professor Daniell (fig. 146). Each cell of this "constant" battery consists of a copper cylinder $3\frac{1}{2}$ inches in diameter, and of a height varying from 6 to 18 inches. The zinc is employed in the form of a rod $\frac{3}{4}$ of an inch in diameter, carefully amalgamated, and suspended in the centre of the cylinder. A second cell of porous

earthenware or animal membrane intervenes between the zinc and the copper: this is filled with a mixture of 1 part by measure of oil of vitriol and 8 of water, and the exterior space with the same liquid, saturated with copper sulphate. A sort of little colander is fitted to the top of the cell, in which crystals of the copper sulphate are placed, so that the strength of the solution may remain unimpaired. When communication is made by a wire between the rod and the cylinder, a powerful current is produced, the power of which may be increased to any extent by connecting a sufficient number of such cells into a series, on the principle of the crown of cups, the copper of the first being attached to the zinc of the second. Ten such alternations constitute a very powerful apparatus, which has the great advantage of retaining its energy undiminished for a long time.

Fig. 146.



By this arrangement of the voltaic battery, the polarization of the copper plate is altogether avoided; the zinc in the porous cell, whilst it dissolves in the sulphuric acid, decomposes it, but does not liberate any hydrogen; for by the progress of the decomposition (see p. 246) up to the boundary of the copper solution, the hydrogen takes the place of the copper, and thus ultimately the copper is precipitated on the copper plate. The copper plate therefore remains in its original state, so long as a sufficient quantity of copper sulphate is present in the solution.

By increasing the generative and reducing the antagonizing chemical affinities, Mr. Grove succeeded in forming the constant nitric acid battery which bears his name. This instrument is capable of producing a far greater degree of power than the battery previously mentioned, and hence it has become one of the most important means of promoting electrical science in the present day. The zinc dips into dilute sulphuric acid; and instead of a solution of copper, concentrated nitric acid is used, which surrounds a platinum plate. It is evident that the electrolytic action which begins at the zinc passes through the sulphuric acid, and in a precisely similar way through the contiguous nitric acid. Hydrogen would thus be liberated on the platinum plate. This action is not rendered visible by the evolution of gas, but only gradually by the change of color in the nitric acid: for the hydrogen liberated by the electrical action forms water at the expense of the oxygen yielded by the nitric acid; and by this means, so long as sufficient nitric acid is present, the purity of the surface of the platinum plate is maintained.

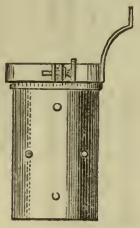
Fig. 147.

One of the cells in this battery is represented in section in fig. 147. The zinc plate is bent round, so as to present a double surface, and well amalgamated: within it stands a thin flat cell of porous earthenware, filled with strong nitric acid, and the whole is immersed in a mixture of 1 part by measure of oil of vitriol and 6 of water, contained either in one of the cells of Wollaston's trough, or in a separate cell of glazed porcelain, made for the purpose. The apparatus is completed by a plate of platinum foil, which dips into the nitric acid, and forms the positive side of the arrangement. With ten such pairs, experiments of decomposition, ignition of wires, the light between charcoal points, &c., can be exhibited with great brilliancy, while the battery itself is very compact and portable, and, to a great extent, constant in its action. The zinc, as in the case of Daniell's battery, is consumed only while the

current passes, so that the apparatus may be arranged an hour or two before it is required for use, which is often a matter of great convenience; and local action from the precipitation of copper on the zinc is avoided.

Professor Bunsen has modified the Grove battery by substituting for the platinum dense charcoal or coke, which is an excellent conductor of electricity. By this alteration, at a very small expense, a battery may be made nearly as powerful and useful as that of Grove. On account of its cheapness, any one may put together one hundred or more of Bunsen's cells, by which the most magnificent phenomena of heat and light may be obtained.

Fig. 148.



The accompanying figure shows the form of the round carbon cylinder, which is used in these cells. It is hollowed so as to receive a porous earthenware cell, in which a round plate of zinc is placed. The upper edge of the cylinder of carbon is well saturated with wax, and is surrounded by a copper ring, by means of which it may be put in connection with the zinc of the adjoining pair.

Bunsen's carbon cylinder is likewise well adapted for the use of dilute sulphuric acid alone, without the addition of nitric acid. It is, however, better to saturate the dilute sulphuric acid with potassium bichromate. When this mixture contains at least double the amount of sulphuric acid which is necessary to decompose the chromate, a battery thus formed surpasses in power the nitric acid battery, but does not furnish currents of the same constancy.

Mr. Smee has contrived an ingenious battery, in which silver, covered with a thin coating of finely divided metallic platinum, is employed in association with amalgamated zinc and dilute sulphuric acid. The rough surface appears to permit the ready disengagement of the bubbles of hydrogen.

Within the last twenty-five years, several very beautiful and successful applications of voltaic electricity have been made, which may be slightly mentioned. Mr. Spencer and Professor Jacobi have employed it in copying, or rather in multiplying, engraved plates and medals, by depositing upon their surfaces a thin coating of metallic copper, which, when separated from the original, exhibits, in reverse, a most faithful representation of the latter. By using this in its turn as a mould or matrix, an absolutely perfect *fac-simile* of the plate or medal is obtained. In the former case, the impressions taken on paper are quite undistinguishable from those directly derived from the work of the artist; and as there is no limit to the number of *electrotype* plates which can be thus produced, engravings of the most beautiful description may be multiplied indefinitely. The copper is very tough, and bears the action of the press perfectly well.

Fig. 149.

The apparatus used in this and many similar processes is of the simplest possible kind. A trough or cell of wood is divided by a porous diaphragm, made of a very thin piece of sycamore, into two parts; dilute sulphuric acid is put on one side, and a saturated solution of copper sulphate, sometimes mixed with a little acid, on the other. A plate of zinc is soldered to a wire or strip of copper, the other end of which is secured by similar means to the engraved copper plate. The latter is then immersed in the solution of sulphate, and the zinc in the acid. To prevent deposition of copper on the back of the copper plate, that portion is covered with varnish. For medals and small works, a porous earthenware cell, placed in a jelly-jar, may be used.

Other metals may be precipitated in the same manner, in a smooth and compact form, by the use of certain precautions which have been gathered by experience. Electro-gilding and plating are now carried on very largely and in great perfection by Messrs. Elkington and others. Even non-conducting bodies, as sealing-wax and plaster of Paris, may be coated with metal; it is only necessary, as Mr. Robert Murray has shown, to rub over them the thinnest possible film of plumbago. Seals may thus be copied in a very few hours with unerring truth.

Becquerel, several years ago, published an exceedingly interesting account of certain experiments in which crystallized metals, oxides, and other insoluble substances had been produced by the slow and continuous action of feeble electrical currents, kept up for months, or even years. These products exactly resemble natural minerals; and, indeed, the experiments throw great light on the formation of the latter within the earth.*

The common but very pleasing experiment of the *lead-tree* is greatly dependent on electro-chemical action. When a piece of zinc is suspended in a solution of lead acetate, the first effect is the decomposition of a portion of the latter, and the deposition of metallic lead upon the surface of the zinc; it is simply a displacement of a metal by a more oxidable one. The change does not, however, stop here; metallic lead is still deposited in large and beautiful plates upon that first thrown down, until the solution becomes exhausted, or the zinc entirely disappears. The first portions of lead form with the zinc a voltaic arrangement of sufficient power to decompose the salt: under the peculiar circumstances in which the latter is placed, the metal is precipitated upon the negative portion — that is, the lead — while the oxygen and acid are taken up by the zinc.

Fig. 150.

Mr. Grove has contrived a battery in which an electrical current, of sufficient intensity to decompose dilute sulphuric acid, is produced by the reaction of oxygen upon hydrogen. Each *element* of this interesting apparatus consists of a pair of glass tubes to contain the gases dipping into a vessel of acidulated water. Both tubes contain platinum plates, covered with a rough deposit of finely divided platinum, and furnished with conducting wires, which pass through the tops or sides of the tubes, and are hermetically sealed into the latter. When the tubes are charged with oxygen on the one side and hydrogen on the other, and the wires connected with a galvanoscope, the needle of the instrument becomes instantly affected; and when ten or more are combined in a series, the oxygen-tube of the one with the hydrogen-tube of the next, &c., while the terminal wires dip into acidulated water, a rapid stream of minute bubbles from either wire indicates the decomposition of the liquid; and when the experiment is made with a small voltameter, it is found that the oxygen and hydrogen disengaged exactly equal in amount the quantities absorbed by the act of combination in each tube of the battery.

Heat developed by the Electric Current. — All parts of the electric circuit, the plates, the liquid in the cells of the battery, the conducting wires, and any electrolytes undergoing decomposition, all become heated during the passage of the current. The rise of temperature in any part of the circuit depends partly on the strength of the current, partly on its resistance, those bodies which offer the greatest resistance, or are the worst conductors, being most strongly heated by a current of given strength. Thus,

* Traité de l'Electricité et du Magnétisme, iii. 239.

when a thick and a thin wire of the same metal are included in the same circuit, the latter becomes most strongly heated, and a platinum wire is much more strongly heated than a silver or copper wire of the same thickness.

By exact experiments it has been found that both in metallic wires and in liquids traversed by an electric current, the evolution of heat is directly proportional: 1st, *to the resistance;* 2d, *to the strength of the current.* Joule has* also shown that the evolution of heat in each couple of the voltaic battery is subject to the same law, which, therefore, holds good in every part of the circuit, including the battery.

The strength of an electric current is measured by the quantity of detonating gas (2 vol. H. to 1 vol. O.) which it can evolve from acidulated water in a given time, and the *unit of current strength is the current which eliminates one cubic centimetre of detonating gas at* 0° C. and 760mm. *barometric pressure in a minute.* Now Lenz has shown that *when a current of the unit of strength passes* through a wire whose resistance is equal to that of a copper wire 1 metre long and 1 millimetre in diameter, it develops a quantity of heat sufficient to raise the temperature of 1 gram of water from 0° to 1° C. in $5\frac{3}{4}$ minutes: and assuming as the unit of heat the quantity required to raise the temperature of 1 gram of water from 0° to 1° C., the law may be thus expressed:

A current of the unit of strength passing through a conductor which exerts the unit of resistance, develops therein 1·057 *heat-units in an hour, or* 0.076 *heat-unit in a minute.*

With a current of a given strength, the sum of the quantities of heat evolved in the battery and in the metallic conductor joining its poles, is constant, the heat actually developed in the one part or the other varying according to the thickness of the metallic conductor. This was first shown by De la Rive, and has been confirmed by Favre.† De la Rive made use of a couple consisting of platinum and distilled zinc or cadmium, excited by pure and very strong nitric acid, the two metals being united by a platinum wire, more or less thick, which was plunged into the same quantity of strong nitric acid contained in a capsule similar to that which held the voltaic couple. By observing the temperatures in the two vessels with delicate thermometers, the sum of these temperatures was found to be constant, the one or the other being greater according to the thickness of the connecting wire.

Favre,‡ by means of a calorimeter, similar to that which he used in his experiments on the development of heat by chemical action, has shown that in a pair of zinc and platinum plates, excited by dilute sulphuric acid and connected by platinum wires of various length and thickness, for every 32·5 grams of zinc dissolved, a quantity of heat is developed in the entire circuit equal to 18,137 heat-units, but variously distributed between the battery-cell and the wire, according to the thickness of the latter. Now this quantity of heat is nearly the same as that which is evolved in the simple solution of 32·5 grams of zinc in dilute sulphuric acid, without the formation of a voltaic circuit, viz. 18,444 units. Hence Favre concludes that the heat developed by the resistance of a metallic or other conductor connecting the poles of the battery is simply borrowed from the total quantity of heat evolved by the chemical action taking place in the battery, and is rigorously complementary to that which remains in the cells of the battery, the heat evolved in the entire circuit being the exact equivalent of the chemical action which takes place. If any external work is performed by the cur-

* Phil. Mag. [3] xix. 210.
† Ann. Ch. Phys. [3] xl. 393.
‡ Comptes Rendus, xlv. 56.

rent, such as electrolysis, or mechanical work, or by an electro-magnetic engine, the heat evolved in the circuit is diminished by the heat-equivalent of the decomposition or mechanical work done.

CRYSTALLIZATION; CRYSTALLINE FORM.

Almost every substance, simple or compound, capable of existing in the solid state, assumes, under favorable circumstances, a distinct geometrical form or figure, usually bounded by plane surfaces, and having angles of fixed and constant value. The faculty of crystallization seems to be denied only to a few bodies, chiefly highly complex organic principles, which stand, as it were, upon the very verge of organization, and which, when in the solid state, are frequently characterized by a kind of beady or globular appearance, well known to microscopical observers.

The most beautiful examples of crystallization are to be found among natural minerals, the results of exceedingly slow changes constantly occurring within the earth. It is invariably found that artificial crystals of salts, and other soluble substances which have been slowly and quietly deposited, surpass in size and regularity those of more rapid formation.

Solution in water or some other liquid is a very frequent method of effecting crystallization. If the substance be more soluble at a high than at a low temperature, then a hot and saturated solution left to cool slowly will generally be found to furnish crystals; this is a very common case with salts and various organic principles. If it be equally soluble, or nearly so, at all temperatures, then slow spontaneous evaporation in the air, or over a surface of oil of vitriol, often proves very effective.

Fusion and slow cooling may be employed in many cases: that of sulphur is a good example: the metals, when thus treated, usually afford traces of crystalline figures, which sometimes become very beautiful and distinct, as with bismuth. A third condition under which crystals very often form is in passing from the gaseous to the solid state, of which iodine affords a good instance. When by any of these means time is allowed for the symmetrical arrangement of the particles of matter at the moment of solidification, crystals are produced.

That crystals owe their figure to a certain regularity of internal structure is shown both by their mode of formation and also by the peculiarities attending their fracture. A crystal placed in a slowly evaporating saturated solution of the same substance grows or increases by a continued deposition of fresh matter upon its sides, in such a manner that the angles formed by the meeting of the latter remain unaltered.

The tendency of most crystals to split in particular directions, called by mineralogists *cleavage*, is a certain indication of regular structure, while the curious optical properties of many among them, and their remarkable mode of expansion by heat, point to the same conclusion.

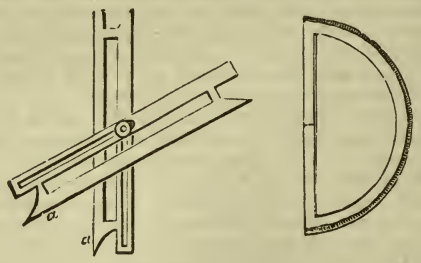
It may be laid down as a general rule that every substance has its own crystalline form, by which it may very frequently be recognized at once — not that each substance has a different figure, although very great diversity in this respect is to be found. Some forms are much more common than others, as the cube and six-sided prism, which are very frequently assumed by a number of bodies not in any way related.

The same substance may have, under different sets of circumstances, as high and low temperatures, two different crystalline forms, in which case it is said to be *dimorphous*. Sulphur and carbon furnish, as already noticed, examples of this curious fact; another case is presented by calcium carbonate in the two modifications of calc spar and arragonite, both chemically the same, but physically different. A fourth example might be given in mercuric iodide, which also has two distinct forms, and even two distinct colors, offering as great a contrast as those of diamond and graphite.

The angles of crystals are measured by means of instruments called *goniometers*, of which there are two kinds in use, namely, the old or common goniometer, and the reflecting goniometer of Dr. Wollaston.

The common goniometer consists of a pair of steel blades moving with friction upon a centre, as shown in fig. 151. The edges *a a* are carefully

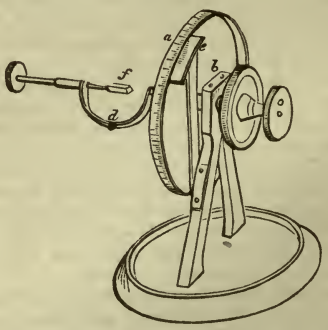
Fig. 151.



adjusted to the faces of the crystal whose inclination to each other it is required to ascertain, and then the instrument being applied to the divided semicircle, the contained angle is at once read off. An approximative measurement, within one or two degrees, can be easily obtained by this instrument, provided the planes of the crystal are tolerably perfect, and large enough for the purpose. Some practice is of course required before even this amount of accuracy can be attained.

The reflecting goniometer is a very superior instrument, its indications being correct within a fraction of a degree: it is applicable also to the measurement of the angles of crystals of very small size, the only condition required being that their planes be smooth and brilliant. The subjoined sketch (fig. 152) will convey an idea of its nature and mode of use.

Fig. 152.

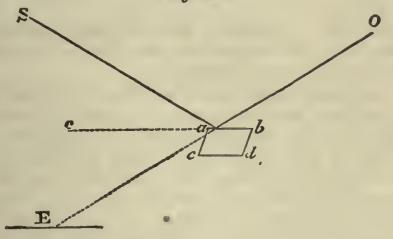


a is a divided circle or disc of brass, the axis of which passes stiffly and without shake through the support *b*. This axis is itself pierced to admit the passage of a round rod or wire, terminated by the milled-edged head *c*, and destined to carry the crystal to be measured, by means of the jointed arm *d*. The crystal at *f* can thus be turned round, or adjusted in any

desired position, without the necessity of moving the disc. A vernier, *e*, immovably fixed to the upright support, serves to measure with great accuracy the angular motion of the divided circle.

The principle upon which the measurement of the angle rests is very simple. If the two adjacent planes of a crystal be successively brought into the same position, the angle through which the crystal will have moved will be *the supplement to that contained between the two planes*. If, for example, in a small crystal, *c a b* (fig. 153) be the angle which is to be determined,

Fig. 153.



and the reflecting surface *a b* be placed in such a position that the reflection of the image of a distant point S seen from O exactly covers a point E lying in the line of the reflected ray, then the other side *a c* of the angle *c a b* must be turned through the angle *c a f*, in order to assume the same position, and to give the same phenomena as the plane *a b* previously did. The angle *c a f* is the supplement of the angle *c a b*. All that is required to be done, therefore, is to measure the angle *c a f* with accuracy, and subtract its value from 180°; and this the goniometer effects.

One method of using the instrument is the following: — The goniometer is placed at a convenient height upon a steady table in front of a well illuminated window. Horizontally across the latter, at the height of eight or nine feet from the ground, is stretched a narrow black ribbon, while a second similar ribbon, adjusted parallel to the first, is fixed beneath the window, a foot or eighteen inches above the floor. The object is to obtain two easily visible black lines, perfectly parallel. The crystal to be examined is attached to the arm of the goniometer at *f* by a little wax, and adjusted in such a manner that the edge joining the two planes whose inclination is to be measured shall nearly coincide with, or be parallel to, the axis of the instrument. This being done, the adjustment is *completed* in the following manner: — The divided circle is turned until the zero of the vernier comes to 180°; the crystal is then moved round by means of the inner axis *c* (fig. 152) until the eye placed near it perceives the image of the upper black line reflected from the surface of one of the planes in question. Following this image, the crystal is still cautiously turned until the upper black line seen by reflection approaches and overlaps the lower black line seen *directly* by another portion of the pupil. It is obvious, that if the plane of the crystal be quite parallel to the axis of the instrument (the latter being horizontal), the two lines will coincide completely. If, however, this should not be the case, the crystal must be moved upon the wax until the two lines fall in one when superposed. The second face of the crystal must then be adjusted in the same manner, care being taken not to derange the position of the first. When by repeated observation it is found that both have been correctly placed, so as to bring the edge into the required condition of parallelism with the axis of motion, the measurement of the angle may be made.

For this purpose the crystal is moved as before by the inner axis until the image of the upper line, reflected from the first face of the crystal, covers the lower line seen directly. The great circle, carrying the whole with it, is then cautiously turned until the same coincidence of the upper with the lower line is seen by means of the second face of the crystal; that is, the second face is brought into exactly the same position as that previously occupied by the first. Nothing then remains but to read off by the vernier the angle through which the circle has been moved in this operation. The division upon the circle itself is very often made *backward*, so that the angle of motion is not obtained, but its supplement, or the angle of the crystal required.

It may be necessary to remark, that, although the principle of the operation described is in the highest degree simple, its successful practice requires considerable skill and experience.

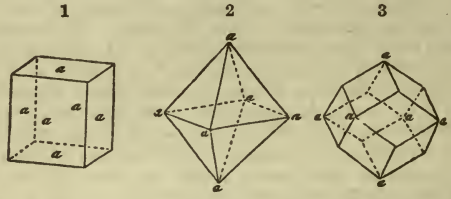
If a crystal of tolerably simple form be attentively considered, it will become evident that certain directions can be pointed out in which straight lines may be imagined to be drawn, passing through the central point of the crystal from side to side, from end to end, or from one angle to that opposed to it, &c., about which lines the particles of matter composing the crystal may be conceived to be symmetrically built up. Such lines, or *axes*, are not always purely imaginary, however, as may be inferred from the remarkable optical properties of many crystals: upon their number, relative lengths, position, and inclination to each other, depends the outward figure of the crystal itself.

All crystalline forms may upon this plan be arranged in six classes or *systems;* these are the following:

1. *The monometric, regular,* or *cubic system.* — The crystals of this division have three equal axes, all placed at right angles to each other. The most important forms are the *cube* (1), the *regular octohedron* (2), and the *rhombic dodecahedron* (3).

The letters *a*—*a* (fig. 154) show the termination of the three axes, placed as stated.

Fig. 154.

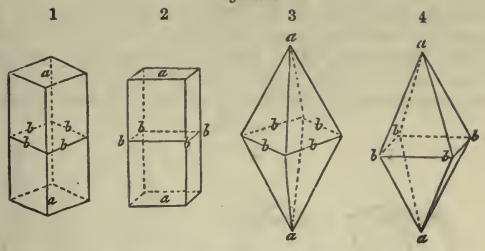


Very many substances, both simple and compound, assume these forms, as most of the metals, carbon in the state of diamond, common salt, potassium iodide, the alums, fluor-spar, iron bisulphide, garnet, spinelle, &c.

2. *The dimetric, quadratic, square prismatic,* or *pyramidal system.* — Three axes are here also observed, at right angles to each other. Of these, however, two only are of equal length, the third being longer or shorter. The most important forms are, a *right square prism*, in which the lateral axes terminate in the central point of each side (1); a *second* right square prism, in which the axes terminate in the edges (2); a corresponding pair of *right, square-based octohedrons* (3 and 4).

Examples of these forms are to be found in zircon, native stannic oxide, apophyllite, yellow potassium ferrocyanide, &c.

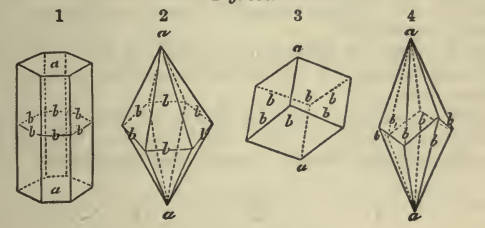
Fig. 155.



a—*a*. Principal or vertical axes.
b—*b*. Secondary or lateral axes.

3. *The rhombohedral system.* — This is very important and extensive; it is characterized by *four* axes, three of which are equal, in the same plane, and inclined to each other at angles of 60°, while the fourth or principal axis is perpendicular to all. The *regular six-sided prism* (1), the *quartz-dodecahedron* (2), the *rhombohedron* (3), and a *second* dodecahedron, called a *scalenohedron*, whose faces are scalene triangles (4), belong to the system in question.

Fig. 156.

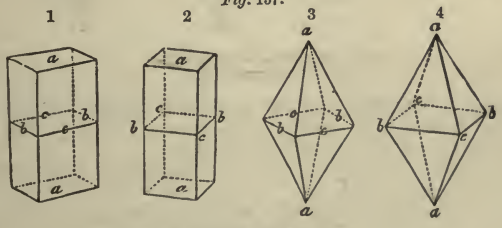


a—*a*. Principal axis.
b—*b*. Secondary axes.

Examples are readily found; as in ice, calc spar, sodium nitrate, beryl, quartz or rock-crystal, and the semi-metals, arsenic, antimony, and tellurium.

4. *The trimetric, rhombic, or right prismatic system.* — This is characterized by three axes of unequal lengths, placed at right angles to each other, as

Fig. 157.



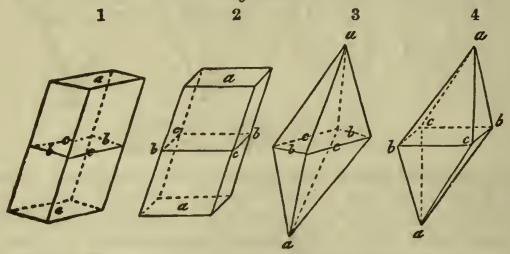
a—*a*. Principal axis,
b—*b*, *c*—*c*. Secondary axes.

in the *right rectangular prism* (1), the *right rhombic prism* (2), the *right rectangular-based octohedron* (3), and the *right rhombic-based octohedron* (4).

The system is exemplified in sulphur crystallized at a low temperature, arsenical iron pyrites, potassium nitrate and sulphate, barium sulphate, &c.

5. *The monoclinic* or *oblique prismatic system.* — Crystals belonging to this group have also three axes, which may be all unequal; two of these (the secondary) are placed at right angles, the third being so inclined as to be oblique to one and perpendicular to the other. To this system may be re-

Fig. 158.



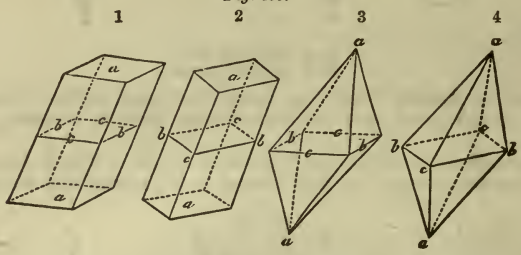
a—*a*. Principal axis.
b—*b*, *c*—*c*. Secondary axes.

ferred the four following forms: *The oblique rectangular prism* (1), the *oblique rhombic prism* (2), the *oblique rectangular-based octohedron* (3), the *oblique rhombic-based octohedron* (4).

Such forms are taken by sulphur crystallized by fusion and cooling, realgar, sulphate, carbonate and phosphate of sodium, borax, green vitriol, and many other salts.

6. *The triclinic, anorthic,* or *doubly oblique prismatic system.* — The crystalline forms comprehended in this division are, from their great apparent irregularity, exceedingly difficult to study and understand. In them are

Fig. 159.



a—*a*. Principal axis, as before.
b—*b*, *c*—*c*. Secondary axes.

traced three axes, which may be all unequal in length, and are all oblique to each other, as in the two *doubly oblique prisms* (1 and 2), and in the corresponding *doubly oblique octohedrons* (3 and 4).

Copper sulphate, bismuth nitrate, and potassium quadroxalate afford illustrations of these forms.

If a crystal increase in magnitude by equal additions on every part, it is quite clear that its figure must remain unaltered; but if, from some cause, this increase should be partial, the newly deposited matter being distributed unequally, but still in obedience to certain definite laws, then alterations of form are produced, giving rise to figures which have a direct geometri-

cal connection with that from which they are derived. If, for example, in the cube, a regular omission of successive rows of particles of matter in a certain order be made at each solid angle, while the crystal continues to increase elsewhere, the result will be the production of small triangular planes, which, as the process advances, gradually usurp the whole of the surface of the crystal, and convert the cube into an octohedron. The new

Fig. 160.

Passage of cube to octohedron.

planes are called *secondary*, and their production is said to take place by regular *decrements* upon the solid angles. The same thing may happen on the edges of the cube; a new figure, the rhombic dodecahedron, is then generated. The modifications which can thus be produced of the original or *primary* figure (all of which are subject to exact geometrical laws) are very numerous. Several distinct modifications may be present at the same time, and thus render the form exceedingly complex.

Crystals often cleave parallel to all the planes of the primary figure, as in calc spar, which offers a good illustration of this perfect cleavage. Sometimes one or two of these planes have a kind of preference over the rest in this respect, the crystal splitting readily in these directions only.

A very curious modification of the figure sometimes occurs by the excessive growth of each alternate plane of the crystal; the rest become at length obliterated, and the crystal assumes the character called *hemihedral* or *half-sided.* This is well seen in the production of the tetrahedron from the regular octohedron, and of the rhombohedric form by a similar change from the quartz-dodecahedron already figured.

Fig. 161.

Passage of octohedron to tetrahedron.

Forms belonging to the same crystallographic system are related to each other by several natural affinities.

1. *It is only the simple forms of the same system that can combine into a complex form.* — For in all fully developed (holohedral) natural crystals it is found that all the similar parts, if modified at all, are modified in an exactly similar manner (in hemihedral forms, half the similar edges and angles alternately situated are similarly modified). Now this can be the case only when the dominant form and the modifying form are developed according to the same law of symmetry. Thus, if a cube and a regular octohedron are developed round the same system of axes, each summit of the cube is cut off to the same extent by a face of the octohedron, or *vice versâ.* But a cube could never combine in this manner with a rhombic octo-

hedron, because it would be impossible to place the two forms in such a manner that similar parts of the one should throughout replace similar parts of the other.

The crystals of each system are thus subject to a peculiar and distinct set of modifications, the observation of which very frequently constitutes an excellent guide to the discovery of the primary form itself.

2. *Crystals belonging to the same system are intimately related in their optical properties.* — Crystals belonging to the regular system (as the diamond, alum, rock-salt, &c.) refract light in the same manner as uncrystallized bodies; that is to say, they have but one refractive index, and a ray of light passing through them in any direction is refracted singly. But all other crystals refract doubly, that is to say, a ray of light passing through them (except in certain directions) is split into two rays, the one, called the *ordinary* ray, being refracted as it would be by an amorphous body, the other, called the *extraordinary* ray, being refracted according to peculiar and more complex laws (see LIGHT). Now the crystals of the *dimetric* and *hexagonal* systems resemble each other in this respect, that in all of them there is one direction, called the optic axis, or axis of double refraction (coinciding with the principal crystallographic axis), along which a ray of light is refracted singly, while in all other directions it is refracted doubly; whereas in crystals belonging to the other systems, viz., the trimetric and the two oblique systems, there are always *two* directions or axes, along which a ray is singly refracted.

3. *Crystals belonging to the same system resemble each other in their mode of conducting heat.* — Amorphous bodies and crystals of the regular system conduct heat equally in all directions, so that, supposing a centre of heat to exist within such a body, the isothermal surfaces will be spheres. But crystals of the dimetric and hexagonal systems conduct equally only in directions perpendicular to the principal axis, so that in such crystals the isothermal surfaces are ellipsoïds of revolution around that axis; and crystals belonging to either of the three other systems conduct unequally in all directions, so that in them the isothermal surfaces are ellipsoïds with three unequal axes.

Relations of Form and Constitution; Isomorphism.

Certain substances, to which a similar chemical constitution is ascribed, possess the remarkable property of exactly replacing each other in crystallized compounds without alteration of the characteristic geometrical figure. Such bodies are said to be *isomorphous.**

For example, magnesia, zinc oxide, cupric oxide, ferrous oxide, and nickel oxide are allied by isomorphic relations of the most intimate nature. The salts formed by these substances with the same acid and similar proportions of water of crystallization, are identical in their form, and, when of the same color, cannot be distinguished by the eye: the sulphates of magnesium and zinc may be thus confounded. These sulphates, too, all combine with potassium sulphate and ammonium sulphate, giving rise to double salts, whose figure is the same, but quite different from that of the simple sulphates. Indeed this connection between identity of form and parallelism of constitution runs through all their combinations.

In the same manner alumina and iron sesquioxide replace each other continually without change of crystalline figure: the same remark may be made of the oxides of potassium, sodium, and ammonium, these bodies being strictly isomorphous. The alumina in common alum may be replaced by iron sesquioxide, the potash by ammonia or by soda, and still the figure of the crystal remains unchanged. These replacements may be partial

* From ἴσος, equal, and μόρφη, shape or form.

only: we may have an alum containing both potash and ammonia, or alumina and chromium sesquioxide. By artificial management — namely, by transferring the crystal successively to different solutions — we may have these isomorphous and mutually replacing compounds distributed in different layers upon the same crystal.

For these reasons, mixtures of isomorphous salts can never be separated by crystallization, unless their difference of solubility is very great. A mixed solution of ferrous sulphate and nickel sulphate, isomorphous salts, yields on evaporation crystals containing both iron and nickel. But if before evaporation the ferrous salt be converted into ferric salt, by chlorine or other means, then the crystals obtained are free from iron, except that of the mother-liquor which wets them. The ferric salt is no longer isomorphous with the nickel salt, and easily separates from the latter.

When compounds are thus found to correspond, it is inferred that the elements composing them are also sometimes isomorphous. Thus, the metals magnesium, zinc, iron, and copper are presumed to be isomorphous: arsenic and phosphorus have not the same crystalline form; nevertheless, they are said to be isomorphous, because arsenic and phosphoric acids give rise to combinations which agree most completely in figure and constitution. The chlorides, iodides, bromides, and fluorides agree, whenever they can be observed, in the most perfect manner: hence the elements themselves are believed to be also isomorphous. Unfortunately, for obvious reasons, it is very difficult to observe the crystalline figure of most of the elementary bodies, and this difficulty is increased by the frequent dimorphism they exhibit.

Absolute identity of value in the angles of crystals is not always exhibited by isomorphous substances. In other words, small variations often occur in the magnitude of the angles of crystals of compounds which in all other respects show the closest isomorphic relations. This should occasion no surprise, as there are reasons why such variations might be expected, the chief perhaps being the unequal effects of expansion by heat, by which the angles of the same crystal are changed by alteration of temperature. A good example is found in the case of the carbonates of calcium, magnesium, manganese, iron, and zinc, which are found native crystallized in the form of obtuse rhombohedrons (fig. 156), not distinguishable from each other by the eye, or even by the common goniometer, but showing small differences when examined by the more accurate instrument of Dr. Wollaston. These compounds are isomorphous, and the measurements of the obtuse angles of their rhombohedrons are as follows:

Calcium carbonate	105° 5′
Magnesium "	107° 25′
Manganous "	107° 20′
Ferrous "	107°
Zinc "	107° 40′

Anomalies in the composition of various earthy minerals, which formerly threw much obscurity upon their chemical nature, have been in great measure explained by these discoveries. Specimens of the same mineral from different localities were found to afford very discordant results on analysis. But the proof once given of the extent to which substitution of isomorphous bodies may go, without destruction of what may be called the primitive type of the compound, these difficulties vanish.

Decision of a doubtful point concerning the constitution of a compound may now and then be very satisfactorily made by a reference to this same law of isomorphism. Thus, alumina, the only known oxide of aluminium, is judged to be a sesquioxide, from its relation to sesquioxide of iron,

which is certainly so; the black oxide of copper is inferred to be really the monoxide, although it contains twice as much oxygen as the red oxide, because it is isomorphous with magnesia and zinc oxide, both undoubted monoxides.

The subjoined table will serve to convey some idea of the most important families of isomorphous elements; it is taken, with slight modification, from Professor Graham's Elements of Chemistry,* to which the pupil is referred for fuller details on this interesting subject:

Isomorphous Groups.

(1.)	(3.)	(6.)
Sulphur	Barium	Sodium
Selenium	Strontium	Silver
Tellurium.	Lead.	Thallium
		Gold
(2.)	(4.)	Potassium
Magnesium	Platinum	*Ammonium.*
Calcium	Iridium	
Manganese	Osmium.	(7.)
Iron		Chlorine
Cobalt	(5.)	Iodine
Nickel	Tin	Bromine
Zinc	Titanium	Fluorine
Cadmium	Zirconium	*Cyanogen.*
Copper	Tungsten	
Chromium	Molybdenum	(8.)
Aluminium	Tantalum	Phosphorus
Glucinum.	Niobium.	Arsenic
		Antimony
		Bismuth
		Vanadium.

A comparison of this table with that on page 236 will show that, in many instances, isomorphous elements exhibit equal equivalence or combining power, and more generally that the isomorphous groups consist either wholly of perissad or wholly of artiad elements. The only apparent exception to this rule is afforded by tantalum and niobium, which, although pentads, are isomorphous with tin, tungsten, and other tetrad and hexad elements.

* Second Am. edition, p. 149.

CHEMISTRY OF THE METALS.

THE metals constitute the second and larger group of elementary bodies. A great number of them are of very rare occurrence, being found only in a few scarce minerals; others are more abundant, and some few almost universally diffused throughout the globe. Some of these bodies are of most importance when in the metallic state; others, when in combination, chiefly as oxides, the metals themselves being almost unknown. Many are used in medicine and in the arts, and are essentially connected with the progress of civilization.

If arsenic be included, the metals amount to fifty in number.

Physical Properties. — One of the most remarkable and striking characters possessed by the metals is their peculiar lustre: this is so characteristic, that the expression metallic *lustre* has passed into common speech. This property is no doubt connected with the extraordinary degree of opacity which the metals present in every instance. The thinnest leaves or plates, and the edges of crystalline laminæ, arrest the passage of light in the most complete manner. An exception to the rule is usually made in favor of gold-leaf, which, when held up to the daylight, exhibits a greenish, and in some cases a purple color, as if it were really endued with a certain degree of translucency: the metallic film is, however, generally so imperfect that it is somewhat difficult to say whether the observed effect may not be in some measure due to multitudes of little holes, many of which are visible to the naked eye; but Faraday's experiments have established the translucency of gold beyond all doubt.

In point of *color*, the metals present a certain degree of uniformity: with two exceptions — viz., copper, which is red, and gold, which is yellow — all these bodies are included between the pure white of silver and the bluish-gray tint of lead: bismuth, it is true, has a pinkish color, and calcium and strontium a yellowish tint, but these tints are very feeble.

The differences of *specific gravity* are very wide, passing from lithium, potassium, and sodium, which are lighter than water, to platinum, which is nearly twenty-one times heavier than an equal bulk of that liquid.

Table of the Specific Gravities of Metals at 15·5° C. (60° F.)

Platinum	21·50
Gold	19·50
Uranium	18·4
Tungsten	17·60
Mercury	13·59
Palladium	11·30 to 11·8
Lead	11·45
Silver	10·50
Bismuth	9·90
Copper	8·96
Nickel	8·80
Cadmium	8·70
Molybdenum	8·63

Cobalt	8·54
Manganese	8·00
Iron	7·79
Tin	7·29
Zinc	6·86 to 7·1
Antimony	6·80
Tellurium	6·11
Arsenic	5·88
Aluminium	2·56 to 2·67
Magnesium	1·75
Sodium	0·972
Potassium	0·865
Lithium	0·593

The property of *malleability*, or power of extension under the hammer, or between the rollers of the flatting-mill, is possessed by certain of the metals to a very great extent. Gold-leaf is a remarkable example of the tenuity to which a malleable metal may be brought by suitable means. The gilding on silver wire used in the manufacture of gold lace is even thinner, and yet presents an unbroken surface. Silver may be beaten out very thin — copper also, but to an inferior extent; tin and platinum are easily rolled out into foil; iron, palladium, lead, nickel, cadmium, the metals of the alkalies, and mercury when solidified, are also malleable. Zinc may be placed midway between the malleable and brittle division; then perhaps bismuth; and, lastly, such metals as antimony and arsenic, which are altogether destitute of malleability.

The specific gravity of malleable metals is usually very sensibly increased by pressure or blows, and the metals themselves are rendered much harder, with a tendency to brittleness. This condition is destroyed and the former soft state restored by the operation of *annealing*, which consists in heating the metal to redness out of contact with air (if it will bear that temperature without fusion), and cooling it quickly or slowly according to the circumstances of the case. After this operation, it is found to possess its original specific gravity.

Ductility is a property distinct from the last, inasmuch as it involves the principle of tenacity, or power of resisting tension. The art of wire-drawing is one of great antiquity: it consists in drawing rods of metal through a succession of trumpet-shaped holes in a steel plate, each being a little smaller than its predecessor, until the requisite degree of fineness is attained. The metal often becomes very hard and rigid in this process, and is then liable to break: this is remedied by annealing. The order of tenacity among the metals susceptible of being easily drawn into wire is the following: it is determined by observing the weights required to break asunder wires drawn through the same orifice of the plate:

Fig. 162.

Iron	Gold
Copper	Zinc
Platinum	Tin
Silver	Lead.

Metals differ as much in *fusibility* as in density. The following table will give an idea of their relations to heat. The melting-points of the metals which fuse only at a temperature above ignition, and that of zinc, are on the authority of the late Professor Daniell, having been observed by the help of his pyrometer before described:

		Melting points. F.	C.
Fusible below a red heat.	Mercury	–39°	–39·44°
	Rubidium	101·3	38·5
	Potassium	144·5	62·5
	Sodium	207·7	97·6
	Lithium	356	180
	Tin	442	227·8
	Cadmium (about)	442	228
	Bismuth	497	258
	Thallium	561	294
	Lead	617	325
	Tellurium — rather less fusible than lead.		
	Arsenic — unknown.		
	Zinc	773	412
	Antimony — just below redness.		

		Melting points. F.	C.
Infusible below a red heat.	Silver	1873°	1023°
	Copper	1996	1091
	Gold	2016	1102
	Cast-iron	2786	1530
	Pure iron, Nickel, Cobalt, Manganese, Palladium — Highest heat of forge.		
	Molybdenum, Uranium, Tungsten, Chromium — Agglomerate, but do not melt in the forge.		
	Titanium, Cerium, Osmium, Iridium, Rhodium, Platinum, Tantalum — Infusible in ordinary blast-furnaces; fusible by oxy-hydrogen blowpipe.		

Some metals acquire a pasty or adhesive state before becoming fluid: this is the case with iron and platinum, and also with the metals of the alkalies. It is this peculiarity which confers the very valuable property of welding, by which pieces of iron and steel are united without solder, and the finely divided metallic sponge of platinum is converted into a solid and compact bar.

Volatility is possessed by certain members of this class, and perhaps by all, could temperatures sufficiently elevated be obtained. Mercury boils and distils below a red heat; potassium, sodium, zinc, magnesium, and cadmium rise in vapor when heated to bright redness; arsenic and tellurium are volatile.

CHEMICAL RELATIONS OF THE METALS.

Metallic combinations are of two kinds — namely, those formed by the union of metals among themselves, which are called alloys, or, where mercury is concerned, amalgams; and those generated by combination with the non-metallic elements, as oxides, chlorides, sulphides, &c. In this latter case, the metallic characters are almost invariably lost.

Alloys. — Most metals are probably, to some extent, capable of existing in a state of combination with each other in definite proportions; but it is difficult to obtain these compounds in a separate condition, since they dissolve in all proportions in the melted metals, and do not generally differ so widely in their melting points from the metals they may be mixed with, as to be separated by crystallization in a definite condition. Exceptions to this rule are met with in the cooling of argentiferous lead, the crystallization of brass, and of gun-metal.

The chemical force capable of being exerted between different metals is for the most part very feeble, and the consequent state of combination is therefore very easily disturbed by the influence of other forces. The stability of such metallic compounds is, however, greater in proportion to the general chemical dissimilarity of the metals they contain. But in all cases of combination between metals, the alteration of physical characters, which is the distinctive feature of chemical combination, does not take place to any great extent. The most unquestionable compounds of metals with metals are still metallic in their general physical characters, and there is no such transmutation of the individuality of their constituents as takes place in the combination of a metal with oxygen, or sulphur, chlorine, &c. The alteration of characters in alloys is generally limited to the color, degree of hardness, tenacity, &c., and it is only when the constituent metals are capable of assuming opposite chemical relations that these compounds are distinguished by great brittleness.

The formation of actual chemical compounds, in some cases, when two metals are melted together, is indicated by several phenomena, viz., the evolution of heat, as in the case of platinum and tin, copper and zinc, &c. The density of alloys differs from that of mere mixtures of the metals. In the solidification of alloys, the temperature does not always fall uniformly, but often remains stationary at particular degrees, which may be regarded as the solidifying points of the compounds then crystallizing. Tin and lead melted together in any proportions always form a compound which solidifies at 187° C. The melting-point of an alloy is often very different from the point of solidification, and it is generally lower than the mean melting point of the constituent metals.

But though metals may combine when melted together, it is doubtful whether they remain combined after the solidification of the mass, and the wide differences between the melting and solidifying points of certain alloys appear to indicate that the existence of these compounds is limited to a certain range of temperature. Matthiessen* regards it as probable that the condition of an alloy of two metals in the liquid state may be either that of — 1. A solution of one metal in another; 2. Chemical combination; 3. Mechanical mixture; or, 4. A solution or mixture of two or all of the above; and that similar differences may obtain as to its condition in the solid state.

The chemical action of reagents upon alloys is sometimes very different from their action upon metals in the separate state: thus, platinum alloyed

* British Association Reports, 1863, p. 97.

with silver is readily dissolved by nitric acid, but is not affected by that acid when unalloyed. On the contrary, silver, which in the separate state is readily dissolved by nitric acid, is not dissolved by it when alloyed with gold in proportions much less than one fourth of the alloy by weight.

COMPOUNDS OF METALS WITH METALLOÏDS. — CLASSIFICATION OF METALS.

A classification of the metals according to their equivalence or atomicity is given in the table on p. 236, each of the classes thus formed being divided into groups, the individual members of which possess certain physical or chemical characters in common.

Class I. — *Monad Metals.* — 1. Among these metals *potassium*, *sodium*, *cæsium*, *rubidium*, and *lithium* are called *alkali-metals*. They are soft, easily fusible, volatile at higher temperatures; combine very energetically with oxygen; decompose water at all temperatures; and form strongly basic oxides, which are very soluble in water, yielding powerfully caustic and alkaline hydrates, from which the water cannot be expelled by heat. Their carbonates are soluble in water, and each metal forms only one chloride. The hypothetical metal *ammonium*, NH_4 (p. 348), is usually added to the list of alkali-metals, on account of the general similarity of its compounds to those of potassium and sodium.

2. *Silver* differs greatly from the alkali-metals in its physical and most of its chemical properties, but it is related to them by the isomorphism of some of its compounds with the corresponding compounds of those metals; thus it forms an alum, similar in form and composition to ordinary potash alum.

Class II. — *Dyad Metals.* — 1. The three metals, *barium*, *strontium*, and *calcium*, form oxides called *alkaline earths*, less soluble in water than the true alkalies, but exhibiting similar taste, causticity, and action on vegetable colors. The metals of this group form but one chloride, *e.g.* $BaCl_2$; their carbonates are insoluble in water, and barium sulphate is also insoluble; strontium and calcium sulphates slightly soluble.

2. The metals of the next group, viz. *glucinum*, *thorinum*, *yttrium*, *erbium*, *lanthanum*, and *didymium*, form oxides called *earths*, which are insoluble in water, and cannot be reduced to the metallic state by hydrogen or carbon; their carbonates are insoluble in water, their sulphates soluble. These metals also form but one chloride, viz. a dichloride. They are all very rare.

3. *Magnesium*, *zinc*, and *cadmium* resemble one another in being volatile at high temperatures, and burning when heated in the air; they decompose water at high temperatures, eliminate hydrogen from dilute acids, and form only one oxide and one chloride, *e.g.* ZnO and $ZnCl_2$. Magnesium was formerly classed as an earth-metal, but it bears a much closer analogy to zinc.

4. *Mercury* and *copper* each form two chlorides and two oxides: mercury, for example, forms the two chlorides, $HgCl_2$ and Hg_2Cl_2, and the two oxides, HgO and Hg_2O. Mercurous chloride (calomel) is represented by the formula $\begin{matrix} Hg—Cl \\ | \\ Hg—Cl \end{matrix}$, and the corresponding oxide by $\begin{matrix} Hg \\ | \\ Hg \end{matrix}>O$. The copper compounds are similarly constituted. These metals do not decompose water at any temperature; they are oxidized by nitric and by strong sulphuric acid. The oxides of mercury are reduced to the metallic state by heat alone; those of copper, by ignition with hydrogen or charcoal.

Class III. — *Triad Metals.* — The only two metals belonging to this class are *thallium* and *gold*. Each of them forms a monochloride and a trichloride, also corresponding oxides, *e.g.* gold chlorides, AuCl and $AuCl_3$; oxides,

Au_2O and Au_2O_3. The mono-compounds of thallium are much more stable than the tri-compounds, and in respect of these compounds thallium exhibits very close analogies with the alkali-metals, forming, for example, an alum isomorphous with common potash alum, and phosphates analogous in composition to the phosphates of sodium.

Class IV. — *Tetrad Metals.* — 1. *Platinum*, *palladium*, *iridium*, *rhodium*, *ruthenium*, and *osmium* form a natural group of metals, occurring together in the metallic state, and resembling each other in many of their properties. Platinum and palladium form dichlorides and tetrachlorides, with corresponding oxides, as, *e.g.*, $PtCl_2$, $PtCl_4$, PtO, PtO_2. Iridium forms a dichloride, a tetrachloride, and an intermediate chloride, Ir_2Cl_6, which may be regarded as a compound of the other two, or as constituted according to the formula $\left|\begin{matrix}IrCl_3\\IrCl_3\end{matrix}\right|$. Ruthenium and osmium form chlorides similar in constitution to those of iridium; rhodium only a dichloride, $RhCl_2$, and a trichloride, Rh_2Cl_6. All these metals form oxides analogous in composition to their chlorides, *e. g.* IrO, Ir_2O_3, IrO_2 and likewise higher oxides, iridium and rhodium forming trioxides, IrO_3 and RhO_3, and osmium and ruthenium forming tetroxides, OsO_4 and RuO_4: whence it might be inferred that iridium and rhodium are hexad, osmium and ruthenium octads; but there are no chlorides corresponding to these oxides, and, as already observed (p. 355), the atomicity of an element cannot be inferred from the composition of its oxides. The metals of the platinum group are not acted upon by nitric acid, but only by chlorine or nitromuriatic acid. With the exception of osmium, they do not oxidize in the air at any temperature, and their oxides are all reducible by heat alone. These metals, together with gold, silver, and mercury, which likewise exhibit the last-mentioned character, are sometimes called *noble metals*.

2. *Tin* and *titanium* are closely related to silicium, each forming a volatile tetrachloride; namely, stannic chloride, $SnCl_4$, and titanic chloride, $TiCl_4$, together with the corresponding oxides. Tin likewise forms the stannous compounds, in which it is bivalent, *e. g.*, $SnCl_2$, SnO; and titanium forms the titanous compounds, in which it is apparently trivalent, but really quadrivalent, like aluminium.

3. *Lead* stands by itself. Its quadrivalence is inferred from the composition of *plumbo-tetrethide*, $Pb(C_2H_5)_4$; but in most of its compounds it is bivalent, forming only one chloride, $PbCl_2$, with corresponding iodide, bromide, and fluoride. It forms also the corresponding oxide, PbO, together with a lower oxide, Pb_2O, and three higher oxides, Pb_3O_4, Pb_4O_5, and PbO_2. Lead is allied to barium and strontium by isomorphism of its sulphate with the sulphates of barium and strontium, and to silver, thallium, and mercury by the sparing solubility of its chloride, which is precipitated by hydrochloric acid from solutions of lead salts.

4. *Zirconium* forms a tetrachloride, $ZrCl_4$, and a dioxide, ZrO_2. *Aluminium* is inferred to be tetradic from its analogy to iron in the ferric compounds, but it forms only one class of salts in which it is apparently trivalent, the chloride being $Al_2Cl_6 = \left|\begin{matrix}AlCl_3\\AlCl_3\end{matrix}\right|$, and the oxide $\left|\begin{matrix}O=Al\\O=Al\end{matrix}\right|>O$. Aluminium and zirconium belong to the class of earth-metals, and will be described in connection with them.

5. The *Iron group* comprises *iron*, *manganese*, *cobalt*, *nickel*, *uranium*, *cerium*, and *indium*. The atomicity of these metals has already been discussed. *Manganese* forms a chloride of somewhat doubtful composition, in which it is apparently septivalent; but the rest do not form any compounds with

monad elements in which they exhibit an equivalent value greater than 4. All these metals decompose water at high temperatures. *Nickel* and *cobalt* are magnetic, like iron, and their salts are isomorphous with the corresponding iron compounds. *Indium* is a very rare metal, which has been but imperfectly examined, but it probably belongs to the same group.

Class V.—*Pentad Metals.*—1. *Arsenic* and *antimony* form trichlorides and pentachlorides analogous to those of phosphorus, also the corresponding oxides. *Bismuth* forms a volatile trichloride, and a dichloride, Bi_2Cl_4, or $\begin{vmatrix} BiCl_2 \\ BiCl_2 \end{vmatrix}$. *Vanadium* was formerly supposed to belong to the tungsten group, but it has lately been shown to be a pentad. Its chlorides are not known, but it forms an oxychloride, $VOCl_3$, analogous to phosphorus oxychloride; also the oxides, V_2O_3 and V_2O_5, analogous to those of phosphorus and arsenic, the latter yielding a series of salts, the vanadates, isomorphous with the phosphates and arsenates of corresponding composition.

2. *Tantalum* and *niobium*, formerly regarded as tetrads, have lately been shown by Marignac to form pentachlorides and pentoxides. The oxides of the pentad metals are, for the most part, of acid character.

Class VI.—*Hexad Metals.*—1. *Chromium* forms a hexfluoride, CrF_6, and a corresponding oxide, CrO_3. It likewise forms two series of compounds, in which it exhibits lower degrees of equivalence, viz., the chromic compounds analogous to the ferric compounds, in which it is apparently trivalent, but really quadrivalent; *e. g.*, chromic chloride, Cr_2Cl_6 or $\begin{vmatrix} Cr''' \\ Cr''' \end{vmatrix} Cl_3$, and the chromous compounds, analogous to the ferrous compounds, in which it is bivalent, *e. g.*, $Cr''Cl_2$, $Cr''O$.

2. *Tungsten* forms a hexchloride, WCl_6, and the corresponding oxide, WO_3. *Molybdenum* is not known to form a chloride higher than $MoCl_4$, but its trioxide, MoO_3, is known; and from the general similarity of the tungsten and molybdenum compounds, the latter metal is inferred to the hexadic.

The metals of the alkalies and alkaline earths, on account of their inferior specific gravity, are often called *light metals;* the others, *heavy metals.*

Metallic Chlorides. — All metals combine with chlorine, and most of them in several proportions, as above indicated, forming compounds which may be regarded as derived from one or more molecules of hydrochloric acid, by substitution of a metal for an equivalent quantity of hydrogen; thus:

From	HCl	are derived	monochlorides	like	KCl
"	H_2Cl_2	"	dichlorides	"	$Ba''Cl_2$
"	H_3Cl_3	"	trichlorides	"	$AuCl_3$
"	H_4Cl_4	"	tetrachlorides	"	$Sn^{iv}Cl_4$, &c. &c.

Hydrochloric acid may, in fact, be regarded as the *type* of chlorides in general.

Several chlorides occur as natural products. Sodium chloride, or common salt, occurs in enormous quantities, both in the solid state as rock-salt, and dissolved in sea-water, and in the water of rivers and springs. Potassium chloride occurs in the same forms, but in smaller quantity; the chlorides of lithium, cæsium, rubidium, and thallium also occur in small

quantities in certain spring waters. Mercurous chloride, Hg_2Cl_2, and silver chloride, AgCl, occur as natural minerals.

1. Chlorides are generally prepared by one or other of the following processes: 1. By acting upon the metal with chlorine gas. Antimony pentachloride and copper dichloride are examples of chlorides sometimes produced in this manner. The chlorides of gold and platinum are usually prepared by acting upon the metals with nascent chlorine, developed by hydrochloric and nitric acids. Sometimes, on the other hand, the metal is in a nascent state, as when titanic chloride is formed by passing a current of chlorine over a heated mixture of charcoal and titanic oxide. The chlorides of aluminium and chromium may be obtained by similar processes.

2. Chlorine gas, by its action upon metallic oxides, drives out the oxygen, and unites with the respective metals to form chlorides. This reaction sometimes takes place at ordinary temperatures, as is the case with silver oxide; sometimes only at a red heat, as is the case with the oxides of the alkalies and alkaline earth-metals. The hydrates and carbonates of these last metals, when dissolved or suspended in hot water and treated with excess of chlorine, are converted, chiefly into chlorides, partly into chlorates.

3. Many metallic chlorides are prepared by acting upon the metals with hydrochloric acid. Zinc, cadmium, iron, nickel, cobalt, and tin dissolve readily in hydrochloric acid, with liberation of hydrogen; copper only in the strong boiling acid; silver, mercury, palladium, platinum, and gold, not at all. Sometimes the metal is substituted, not for hydrogen, but for some other metal. Stannous chloride, for instance, is frequently made by distilling metallic tin with mercuric chloride; thus: $2HgCl_2 + Sn_2 = 2SnCl_2 + Hg_2$.

4. By dissolving a metallic oxide, hydrate, or carbonate in hydrochloric acid.

All monochlorides and dichlorides are soluble in water, excepting silver chloride, AgCl, and mercurous chloride, Hg_2Cl_2; lead chloride, $PbCl_2$, is sparingly soluble; these three chlorides are easily formed by precipitation. Many metallic chlorides dissolve also in alcohol and in ether.

Most monochlorides, dichlorides, and trichlorides volatilize at high temperatures without decomposition: the higher chlorides, when heated, give off part of their chlorine. Some chlorides which resist the action of heat alone are decomposed by ignition in the air, yielding metallic oxides and free chlorine: this is the case with the dichlorides of iron and manganese; but most dichlorides remain undecomposed, even in this case. All metallic chlorides, excepting those of the alkali-metals and earth-metals, are decomposed at a red heat by hydrogen gas, with formation of hydrochloric acid: in this way, metallic iron may be obtained in fine cubical crystals. Silver chloride placed in contact with metallic zinc or iron, under dilute sulphuric or hydrochloric acid, is reduced to the metallic state by the nascent hydrogen.

Sulphuric, phosphoric, boric, and arsenic acids decompose most metallic chlorides, sometimes at ordinary, sometimes at higher temperatures. All metallic chlorides, heated with lead dioxide or manganese dioxide and sulphuric acid, give off chlorine, *e. g.*:

$$\underset{\text{Sodium chloride.}}{2NaCl} + \underset{\text{Manganese dioxide.}}{MnO_2} + \underset{\text{Sulphuric acid.}}{2SO_4H_2} = \underset{\text{Sodium sulphate.}}{SO_4Na_2} + \underset{\text{Manganous sulphate.}}{SO_4Mn} + 2OH_2 + Cl_2.$$

Chlorides distilled with sulphuric acid and potassium chromate, yield a dark bluish-red distillate of chromic oxychloride. Some metallic chlorides are decomposed by *water*, forming hydrochloric acid and an oxychloride, *e. g.*: $BiCl_3 + OH_2 = 2HCl + BiClO$. The chlorides of antimony and

stannous chloride are decomposed in a similar manner. All soluble chlorides give with solution of *silver nitrate*, a white precipitate of silver chloride, easily soluble in ammonia, insoluble in nitric acid. With *mercurous nitrate*, they yield a white curdy precipitate of mercurous chloride, blackened by ammonia; and with *lead-salts*, not too dilute, a white crystalline precipitate of lead chloride, soluble in excess of water.

Metallic chlorides unite with each other and with the chlorides of the non-metallic elements, forming such compounds as potassium chloromercurate, $2KCl.HgCl_2$, sodium chloroplatinate, $2NaCl.PtCl_4$, potassium chloriodate, KCl,ICl_3, &c. Metallic chlorides combine in definite proportions with ammonia and organic bases; the chlorides of platinum form with ammonia the compounds $2NH_3.PtCl_2$, $4NH_3.PtCl_2$, $2NH_3.PtCl_4$, and $4NH_3.PtCl_4$; mercuric chloride forms with aniline the compound $2C_6H_7N.HgCl_2$, &c.

Chlorides also unite with oxides and sulphides, forming *oxychlorides* and *oxysulphides*, which may be regarded as chlorides having part of their chlorine replaced by an equivalent quantity of oxygen or sulphur (Cl_2 by O or S). Bismuth, for example, forms an oxychloride having the composition $Bi'''ClO$ or $BiCl_3.Bi_2O_3$.

Bromides. — Bromine unites directly with most metals, forming compounds analogous in composition to the chlorides, and resembling them in most of their properties. The bromides of the alkali-metals occur in sea-water and in many saline springs; silver bromide occurs as a natural mineral. Nearly all bromides are soluble in water, and may be formed by treating an oxide, hydrate, or carbonate, with hydrobromic acid, the solutions when evaporated giving off water for the most part, and leaving a solid metallic bromide; some of them, however, namely, the bromides of magnesium, aluminium, and the other earth-metals, are more or less decomposed by evaporation, giving off hydrobromic acid, and leaving a mixture of metallic bromide and oxide. Silver bromide and mercurous bromide are insoluble in water, and lead bromide is very sparingly soluble; these are obtained by precipitation.

Metallic bromides are solid at ordinary temperatures; most of them fuse at a moderate heat, and volatilize at higher temperatures. The bromides of gold and platinum are decomposed by mere exposure to heat; many others give up their bromine when heated in contact with the air. *Chlorine*, with the aid of heat, drives out the bromine and converts them into chlorides. *Hydrochloric acid* also decomposes them at a red heat, giving off hydrobromic acid. Strong *sulphuric* or *nitric acid* decomposes them, with evolution of hydrobromic acid, which, if the sulphuric or nitric acid is concentrated and in excess, is partly decomposed, with separation of bromine and formation of sulphurous oxide or nitrogen dioxide. Bromides heated with *sulphuric acid* and *manganese dioxide* or *potassium chromate*, give off free bromine.

Bromides in solution are easily decomposed by chlorine, either in the form of gas or dissolved in water, the liquid acquiring a red or reddish-yellow color, according to the quantity of bromine present; and on agitating the liquid with ether, that liquid dissolves the bromine, forming a red solution, which rises to the surface.

Soluble bromides give with *silver nitrate* a white precipitate of silver bromide, greatly resembling the chloride, but much less soluble in ammonia, insoluble in hot nitric acid. *Mercurous nitrate* produces a yellowish-white precipitate; and *lead acetate*, a white precipitate much less soluble in water than the chloride. *Palladium nitrate* produces in solutions of bromides not containing chlorine, a black precipitate of bromide. Palladium chloride produces no precipitate; neither does the nitrate, if soluble chlorides are present.

Bromides unite with each other in the same manner as chlorides; also with oxides, sulphides, and ammonia.

Iodides. — These compounds are obtained by processes similar to those which yield the chlorides and bromides. Many metals unite directly with iodine. Potassium and sodium iodides exist in sea-water and in many salt springs; silver iodide occurs as a natural mineral.

Metallic iodides are analogous to the bromides and chlorides in composition and properties. But few of them are decomposed by heat alone; the iodides of gold, silver, platinum, and palladium, however, give up their iodine when heated.

Most metallic iodides are perfectly soluble in water; but lead iodide is very slightly soluble, and the iodides of mercury and silver are quite insoluble.

Solutions of iodides evaporated out of contact of air, generally leave anhydrous metallic iodides, which partly separate in the crystalline form before the water is wholly driven off. The iodides of the earth-metals, however, are resolved, on evaporation, into the earthy oxides and hydriodic acid, which escapes. A very small quantity of *chlorine* colors the solution yellow or brown, by partial decomposition; and a somewhat larger quantity takes up the whole of the metal, forming a chloride, and separates the iodine, which then gives a blue color with starch; a still larger quantity of chlorine gives the liquid a paler color, and converts the separated iodine into trichloride of iodine, which does not give a blue color with starch, and frequently enters into combination with the metallic chloride produced. Strong *sulphuric acid* and somewhat concentrated *nitric acid* color the solution yellow or brown; and if the quantity of the iodide is large, and the solution much concentrated or heated, they liberate iodine, which partly escapes in violet vapors. *Starch* mixed with the solution, even if it be very dilute, is turned blue — permanently, when the decomposition is effected by sulphuric acid; for a time only when it is effected by nitric acid, especially if that acid be added in large quantity.

The aqueous solution of an iodide gives a brown precipitate with salts of *bismuth;* orange-yellow with lead-salts; dirty-white with cuprous salts, and also with *cupric* salts, especially on the addition of sulphurous acid; greenish-yellow with *mercurous* salts; scarlet with *mercuric* salts; yellowish-white with *silver* salts; lemon-yellow with *gold* salts; brown with platinic salts — first, however, turning the liquid dark brown-red; and black with salts of *palladium*, even when extremely dilute. All these precipitates consist of metallic iodides, many of them soluble in excess of the soluble iodide: the silver precipitate is insoluble in nitric acid and very little soluble in ammonia.

Metallic iodides unite with one another, forming double iodides, analogous to the double chlorides; they also absorb ammonia gas in definite proportions. Some of them, as those of antimony and tellurium, unite with the oxides of the corresponding metals, forming oxyiodides.

Fluorides. — These compounds are formed: 1. By heating hydrofluoric acid with certain metals. — 2. By the action of that acid on metallic oxides. — 3. By heating electro-negative metals — antimony, for example — with fluoride of lead or fluoride of mercury. — 4. Volatile metallic fluorides may be prepared by heating fluor-spar with sulphuric acid and the oxide of the metal.

Fluorides have no metallic lustre; most of them are easily fusible, and for the most part resemble the chlorides. They are not decomposed by ignition, either alone or when mixed with charcoal. When ignited in contact with the air, in a flame which contains aqueous vapor, many of them are converted into oxides, while the fluorine is given off as hydrofluoric acid.

All fluorides are decomposed by *chlorine* and converted into chlorides. They are not decomposed by *phosphoric oxide*, unless silica is present. They are decomposed at a gentle heat by strong *sulphuric acid*, with formation of a metallic sulphate and evolution of hydrofluoric acid.

The fluorides of tin and silver are easily soluble in water; those of potassium, sodium, and iron are sparingly soluble; those of strontium and cadmium very slightly soluble, and the rest insoluble. The solutions of ammonium, potassium, and sodium fluoride have an alkaline reaction. The aqueous solutions of fluorides corrode glass vessels in which they are kept or evaporated. They form with soluble *calcium-salts* a precipitate of calcium fluoride, in the form of a transparent jelly, which is scarcely visible, because its refractive power is nearly the same as that of the liquid; the addition of ammonia makes it plainer. This precipitate, if it does not contain silica, dissolves with difficulty in hydrochloric or nitric acid, and is re-precipitated by ammonia. The aqueous fluorides give a pulverulent precipitate with lead acetate.

The fluorides of antimony, arsenic, chromium, mercury, niobium, osmium, tantalum, tin, titanium, tungsten, and zinc, are volatile without decomposition.

Fluorine has a great tendency to form double salts, consisting of a fluoride of a basic or positive metal united with the fluoride of hydrogen, boron, silicon, tin, titanium, zirconium, &c., *e. g.*:

Potassium hydrofluoride . . .	KHF_2	$= KF.HF$.
Potassium borofluoride . . .	KBF_4	$= KF.BF_3$.
Potassium silicofluoride . . .	K_2SiF_6	$= 2KF.SiF_4$.
Potassium titanofluoride . . .	K_2TiF_6	$= 2KF.TiF_4$.
Potassium stannofluoride . . .	K_2SnF_6	$= 2KF.SnF_4$.
Potassium zircofluoride . . .	K_2ZrF_6	$= 2KF.ZrF_4$.

The four classes of compounds just described, the chlorides, bromides, iodides, and fluorides, form a group often designated as *haloïd compounds* or *haloïd* salts*, from their analogy to sodium chloride or sea-salt, which may be regarded as a type of them all. The elements, chlorine, bromine, iodine, and fluorine, are called *halogens*.

Cyanides. — Closely related to these haloïd compounds are the cyanides, formed by the union of metals with the group CN, cyanogen, which is a monatomic radical derived from the saturated molecule, $C^{iv}N'''H$ (hydrocyanic acid), by abstraction of H.; in short, the cyanides may be regarded as chlorides having the element Cl replaced by the compound radical CN.

Some metals — potassium among the number — are converted into cyanides by heating them in cyanogen gas or vapor of hydrocyanic acid. The cyanides of the alkali-metals are also formed (together with cyanates) by passing cyanogen gas over the heated hydrates or carbonates of the same metals; potassium cyanide also, by passing nitrogen gas over a mixture of charcoal and hydrate or carbonate of potassium at a bright-red heat. Cyanides are formed abundantly when nitrogenous organic compounds are heated with fixed alkali. Other modes of formation will be mentioned hereafter.

The cyanides of the alkali-metals and of barium, strontium, calcium, magnesium, and mercury, are soluble in water, and may be produced by treating the corresponding oxides or hydrates with hydrocyanic acid. Nearly all other metallic cyanides are insoluble, and are obtained by precipitation from the soluble cyanides.

The cyanides of the alkali-metals sustain a red heat without decomposition, provided air and moisture be excluded. The cyanides of many of the

* From ἅλς, the sea.

heavy metals, as lead, iron, cobalt, nickel, and copper, under these circumstances, give off all their nitrogen as gas, and leave a metallic carbonate; mercuric cyanide is resolved into mercury and cyanogen gas; silver cyanide gives off half its cyanogen as gas. Most cyanides, when heated with dilute acids, give off their cyanogen as hydrocyanic acid.

Cyanides have a strong tendency to unite with one another, forming *double cyanides*. The most important of these are the double cyanides of iron and potassium, namely, *potassio-ferrous cyanide* $Fe''K_4(CN)_6$, commonly called yellow prussiate of potash; and *potassio-ferric cyanide*, $Fe'''K_3(CN)_6$, commonly called red prussiate of potash. Both these are splendidly crystalline salts, which dissolve easily in water, and form highly characteristic precipitates with many metallic salts. These salts, with the other cyanides, will be more fully described under "Organic Chemistry;" but they are mentioned here, on account of their frequent use in the qualitative analysis of metallic solutions.

Oxides.—All metals combine with oxygen, and most of them in several proportions. In almost all cases oxides are formed corresponding in composition to the chlorides, one atom of oxygen taking the place of two atoms of chlorine. Many metals also form oxides to which no chlorine analogues are known; thus, lead, which forms only one chloride, $PbCl_2$, forms, in addition to the monoxide, PbO, a dioxide, PbO_2, besides oxides of intermediate composition; osmium also, the highest chloride of which is $OsCl_4$, forms, in addition to the dioxide, a trioxide and a tetroxide. This arises from the fact that any number of atoms of oxygen or other dyad element may enter into a compound without disturbing the balance of equivalency (p. 235).

Just as chlorides are derived by substitution from hydrochloric acid, HCl (p. 304), so likewise may oxides be derived from one or more molecules of water, H_2O; but as the molecule of water contains two hydrogen-atoms, the replacement of the hydrogen may, as already explained (p. 223), be either total or partial, the product in the first case being an anhydrous metallic oxide, and in the second a hydrated oxide or hydrate, in which the oxygen is associated both with hydrogen and with metal; in this manner the following hydrates and anhydrous oxides may be constituted:

Type.	Hydrates.	Oxides.
H_2O	KHO	K_2O
		$Ba''O$
H_4O_2	$Ba''H_2O_2$	$Sn^{iv}O_2$
	$Bi'''HO_2$	
H_6O_3	As^vHO_3	Sb'''_2O_3
	$Sn^{iv}H_2O_3$	$W^{vi}O_3$
H_8O_4	$Zr^{iv}H_4O_4$	$Os^{viii}O_4$
$H_{10}O_5$		$Sb^v_2O_5$.

It may be observed that the hydrates of artiad metals contain the elements of a molecule of the corresponding anhydrous oxide, and of one or more molecules of water; thus:

Barium hydrate	$Ba''H_2O_2 = Ba''O.H_2O$
Stannic hydrate	$Sn^{iv}H_2O_3 = Sn^{iv}O_2.H_2O$
Zirconium hydrate	$Zr^{iv}H_4O_4 = Zr^{iv}O_2.2H_2O$.

But the hydrate of a perissad metal contains in its molecule only half the number of atoms required to make up a molecule of oxide together with a molecule of water; thus;

Potassium hydrate	$KHO = \frac{1}{2}(K_2O.H_2O)$
Bismuth hydrate	$Bi'''HO_2 = \frac{1}{2}(Bi'''_2O_3.H_2O)$
Arsenic hydrate	$As^vHO_3 = \frac{1}{2}(As^v_2O_5.H_2O)$.

These perissad hydrates cannot, therefore, be correctly regarded as compounds of anhydrous oxide and water.

Many metallic oxides occur as natural minerals, and some, especially those of iron, tin, and copper, in large quantities, forming ores from which the metals are extracted.

All metals, except gold, platinum, iridium, rhodium, and ruthenium, are capable of uniting directly with oxygen. Some, as potassium, sodium, and barium, oxidize rapidly on exposure to the air at ordinary temperatures, and decompose water with energy. Most metals, however, when in the massive state, remain perfectly bright and unacted on in dry air or oxygen gas, but oxidize slowly when moisture is present; such is the case with iron, zinc, and lead. Some of the ordinarily permanent metals, when in a very finely divided state, as lead when obtained by ignition of its tartrate, and iron reduced from its oxide by ignition in hydrogen gas, take fire and oxidize spontaneously as soon as they come in contact with the air. Lead, iron, copper, and the volatile metals, arsenic, antimony, zinc, cadmium, and mercury, are converted into oxides when heated in air or oxygen. Many metals, especially at a red heat, are readily oxidized by water or steam. A very general method of preparing metallic oxides is to subject the corresponding hydrates, carbonates, nitrates, sulphates, or any oxygen-salts containing volatile acids, to the action of heat.

Oxides are for the most part opaque earthy bodies, destitute of metallic lustre. The majority of them are fusible; those of lead and bismuth at a low red heat; those of copper and iron at a white heat; those of barium and aluminium before the oxy-hydrogen blowpipe; while calcium oxide (lime) does not fuse at any temperature to which it has yet been subjected. Oxides are, for the most part, much less fusible than the uncombined metals. Osmium tetroxide, and the trioxides of arsenic and antimony, are readily volatile.

A greater or less degree of heat effects the decomposition of many metallic oxides. Those of gold, platinum, silver, and mercury are reduced to the metallic or reguline state by an incipient red heat. At a somewhat higher temperature, the higher oxides of barium, cobalt, nickel, and lead are reduced to the state of monoxides; while the tri-metallic tetroxides of manganese and iron, Mn_3O_4 and Fe_3O_4, are produced by exposing manganese dioxide, MnO_2, and iron sesquioxide, Fe_2O_3, respectively to a still stronger heat. By gentle ignition, arsenic pentoxide is reduced to the state of trioxide, and chromium trioxide to sesquioxide.

The superior oxides of the metals are easily reduced to a lower state of oxidation by treatment with a current of hydrogen gas at a more or less elevated temperature. At a higher degree of heat, hydrogen gas will transform to the reguline state all metallic oxides except the sesquioxides of aluminium and chromium, and the monoxides of manganese, magnesium, barium, strontium, calcium, lithium, sodium, and potassium. The temperature necessary to enable hydrogen to effect the decomposition of some oxides is comparatively low. Thus even metallic iron may be reduced from its oxides by hydrogen gas at a heat considerably below redness, so as to form an iron pyrophorus. Carbon, at a red or white heat, is a still more powerful deoxidating agent than hydrogen, and seems to be capable of completely reducing all metallic oxides whatsoever. The oxidizable metals in general act as reducing agents.

Chlorine decomposes all metallic oxides, except those of the earth-metals, converting them into chlorides, and expelling the oxygen. With silver oxide this reaction takes place at ordinary temperatures; with the alkalies and alkaline earths, at a full red heat. *Sulphur*, at high temperatures, can decompose most metallic oxides. With many oxides, those of silver, mercury, lead, and copper, for instance, metallic sulphides and sulphur diox-

ide are produced. With the highly basylous oxides, the products are metallic sulphate and sulphide. There are some oxides upon which sulphur exerts no action. Of these the principal are magnesia, alumina, chromic, stannic, and titanic oxides. By boiling sulphur with soluble hydrates, mixtures of polysulphide and hyposulphite are produced. With the exception of magnesia, alumina, and chromic oxide, most metallic oxides can absorb sulphuretted hydrogen, to form metallic sulphide or sulph-hydrate, and water.

Oxygen-salts, or Oxysalts. — It has been already explained in the chapter on Oxygen (p. 133), that oxides may be divided into three classes, *acid*, *neutral*, and *basic;* the first and third being capable of uniting with one another in definite proportions, and forming compounds called *salts*. The most characteristic of the acid oxides are those of certain metalloïds, as nitrogen, sulphur, and phosphorus, which unite readily with water or the elements of water, forming compounds called *oxygen-acids*, distinguished by sour taste, solubility in water, and the power of reddening certain vegetable blue colors. The most characteristic of the basic oxides, on the other hand, are those of the alkali-metals and alkaline earth-metals (p. 271), which likewise dissolve in water, but form alkaline solutions, possessing in an eminent degree the power of *neutralizing* acids and forming salts with them. The same power is exhibited more or less by the monoxides of most other metals, as zinc, iron, copper, manganese, &c., and by the sesquioxides of aluminium, iron, chromium, and others. The higher oxides of several of these metals — the trioxide of chromium, for example — exhibit acid characters, being capable of forming salts with the more basic oxides; and some metals, as arsenic, antimony, niobium, and tantalum, form only acid oxides.

In some cases salts are formed by the direct combination of an acid and a basic oxide. Thus, when vapor of sulphuric oxide, SO_3, is passed over red-hot barium oxide, BaO, the two combine together and form barium-sulphate, $SO_3.BaO$ or SO_4Ba. Silicic oxide, SiO_2, phosphoric oxide, P_2O_5, arsenic oxide, As_2O_5, boric oxide, B_2O_3, and other acid oxides capable of withstanding a high temperature without decomposing or volatilizing, likewise unite with basic oxides when heated with them, and form salts.

But in the majority of cases metallic salts are formed by substitution or interchange of a metal for hydrogen, or of one metal for another. It is clear, indeed, that any metallic salt (zinc-sulphate, $SO_3.ZnO$, for example) may be derived from the corresponding acid or hydrogen-salt ($SO_3.H_2O$) by substitution of a metal for an equivalent quantity of hydrogen. Accordingly, metallic salts are frequently produced by the action of an acid on a metal, or a metallic oxide or hydrate, thus:

(1) SO_4H_2 (Hydrogen sulphate.) + Zn'' = SO_4Zn'' (Zinc sulphate.) + H_2.

(2) $2NO_3H$ (Hydrogen nitrate.) + OAg_2 (Silver oxide.) = $2NO_3Ag$ (Silver nitrate.) + OH_2 (Water.)

(3) NO_3H (Hydrogen nitrate.) + OKH (Potassium hydrate.) = NO_3K (Potassium nitrate.) + OH_2 (Water.)

In the instances represented by these equations, the metallic salts formed are soluble in water. Insoluble salts are frequently prepared by interchange of the metals between two soluble salts; thus:

(4) $(NO_3)_2Ba''$ (Barium nitrate.) + SO_4Na_2 (Sodium sulphate.) = SO_4Ba'' (Barium sulphate.) + $2NO_3Na$ (Sodium nitrate.)

In this case the barium sulphate, being insoluble, is precipiated, while the sodium nitrate remains in solution.

In all these reactions, hydrochloric acid, or a metallic chloride, might be substituted for the oxygen-acid or oxygen-salt without the slightest alteration in the mode of action, the product formed in each case being a chloride instead of a nitrate or sulpate; thus:

(1)′	2HCl	+	Zn″	=	$ZnCl_2$	+	H_2
(2)′	2HCl	+	OAg_2	=	2AgCl	+	OH_2
(3)′	HCl	+	OKH	=	KCl	+	OH_2
(4)′	NO_3Ag	+	NaCl	=	AgCl	+	NO_3Na.

From all these considerations it appears that oxygen-salts may be regarded, either as compounds of acid oxides with basic oxides, or as analogous in composition to chlorides, — that is to say, as compounds of a metal with a radical or group of elements, such as NO_3 (*nitrione*) in the nitrates, SO_4 (*sulphione*) in the sulphates, discharging functions similar to those of chlorine, and capable, like that element, of passing unchanged from one compound to another.

For many years, indeed, it was a subject of discussion among chemists whether the former or the latter of these views should be regarded as representing the *actual* constitution of oxygen-salts. Berzelius divided salts into two classes: (1). *Haloïd salts*, comprising, as already mentioned, the chlorides, bromides, iodides, and fluorides, which are compounds of a metal with a monad metallic element. (2). *Amphid salts*, consisting of an acid or electro-negative oxide, sulphide, selenide, or telluride, with a basic or electro-positive compound of the same kind; such as potassium arsenate, $P_2O_5.3OK_2$; potassium sulpharsenate, $P_2S_5.3SK_2$; potassium seleniophosphate, $P_2Se_5.2SeK_2$, &c.

Davy, on the other hand, observing the close analogy between the reactions of chlorides, on the one hand, and of oxygen-salts, such as sulphates, nitrates, &c., on the other, suggested that the latter might be regarded, like the former, as compounds of metals with acid or electro-negative radicals, the only difference being, that in the former the acid-radical is an elementary body, Cl, Br, &c., whereas in the former it is a compound, as SO_4, NO_3, PO_4, &c. This was called the *binary theory of salts;* it was supported by many ingenious arguments by its proposer and several contemporary chemists; in later years also by Liebig, and by Daniell and Miller, who observed that the mode of decomposition of salts by the electric current is more easily represented by this theory than by the older one (p. 247).

At the present day, the relative merits of these two theories are not regarded as a point of very great importance. Chemists, in fact, no longer attempt to construct formulæ which shall represent the actual arrangements of atoms in a compound, the formulæ now in use being rather intended to exhibit, first, the balance or neutralization of the units of equivalency or atomicity of the several elements contained in a compound (p. 231); and, secondly, the manner in which any compound or group of atoms splits up into subordinate groups under the influence of different reagents. According to the latter view, a compound containing three or more elementary atoms may be represented by different formulæ corresponding to the several ways in which it decomposes. Thus hydrogen sulphate or sulphuric acid, SO_4H_2, may be represented by either of the following formula: —

(1.) $SO_4.H_2$, which represents the separation of hydrogen and formation of a metallic sulphate by the action of zinc, &c.: this is the formula corresponding to the binary theory of salts.

(2.) $SO_3.OH_2$. This formula represents the formation of the acid by direct hydration of sulphuric oxide; the separation of water and formation

of a metallic sulphate by the action of magnesia and other anhydrous oxides; and the separation of sulphuric oxide and formation of phosphoric acid by the action of phosphoric oxide:

$$SO_3.OH_2 + MgO = SO_3.MgO + OH_2$$
$$SO_3OH_2 + P_2O_5 = P_2O_5.OH_2 + SO_3.$$

(3.) $SO_2.O_2H_2$, or $SO_2(OH)_2$. This formula represents such reactions as the elimination of hydrogen dioxide by the action of barium dioxide, BaO_2.

(4.) SH_2O_4. This formula represents the formation of sulphuric acid by direct oxidation of hydrogen sulphide SH_2, and the elimination of the latter by the action of ferrous sulphide:

$$SH_2.O_4 + FeS = SO_4Fe + SH_2.$$

Formulæ of the third of these types, like $SO_2(OH)_2$, which represent oxygen-acids as compounds of hydroxyl with certain acid radicals, as SO_2'' (sulphuryl), CO'' (carbonyl), PO''' (phosphoryl), &c., correspond to a great variety of reactions, and are of very frequent use. They exhibit in particular the relation of the oxygen-acids (hydroxylates) to the corresponding chlorides, *e. g.*:

$(SO_2)''(OH)_2$	$(SO_2)''Cl_2$
Sulphuric acid.	Sulphuric chloride.
$(PO)'''(OH)_3$	$(PO)'''Cl_3$
Phosphoric acid.	Phosphoric chloride.

Basicity of Acids. Normal, Acid and Double Salts. — Acids are monobasic, bibasic, tribasic, &c., according as they contain one or more atoms of hydrogen replaceable by metals; thus nitric acid, NO_3H, and hydrochloric acid, ClH, are monobasic; sulphuric acid, SO_4H_2, is bibasic; phosphoric acid, PO_4H_3, is tribasic.

Monobasic acids form but one class of salts by substitution, the metal taking the place of the hydrogen in one, two, or three molecules of the acid, according to its equivalent value or atomicity; thus the action of hydrochloric acid on sodium, zinc, and aluminum is represented by the equations:

$$ClH + Na = ClNa + H,$$
$$2ClH + Zn'' = Cl_2Zn'' + H_2$$
$$3ClH + Al''' = Cl_3Al''' + H_3,$$

and that of nitric acid on the hydrates of the same metals by the equations:

$$NO_3H + Na(HO) = NO_3Na + H(HO)$$
$$2NO_3H + Ba''(HO)_2 = (NO_3)_2Ba'' + 2H(HO)$$
$$3NO_3H + Al'''(HO)_3 = (NO_3)_3Al''' + 3H(HO).$$

Bibasic acids, on the other hand, form two classes of salts, viz. *monometallic* or *acid salts*, in which half the hydrogen is replaced by a metal; and *bimetallic salts*, in which the whole of the hydrogen is thus replaced, the salt being called *normal* or *neutral* if it contains one metal, and *double* if it contains two metals; thus:

From	SO_4H_2	is derived SO_4KH	hydro-potassic or acid potassium sulphate.
"	"	" SO_4K_2	bipotassic or normal potassium sulphate.
"	"	" SO_4Ba''	barium sulphate.
"	$2SO_4H_2$	" $(SO_4)_2K_3Na$	sodio-tripotassic sulphate.
"	"	" $(SO_4)_2Al'''K$	potassio-aluminic sulphate.
"	$3SO_4H_2$	" $(SO_4)_3Al'''_2$	normal aluminium sulphate.

Tribasic acids in like manner form two classes of acid salts, *mono-metallic* or *bimetallic*, according as one third or two thirds of the hydrogen is replaced by a *metal;* also *normal* and *double* or *triple salts*, in which the hydrogen is wholly replaced by one or more metals; in quadribasic acids the variety is of course still greater.

The use of the terminations *ous* and *ic*, as applied to salts, has already been explained. We have only further to observe in this place that when a metal forms but one class of salts, it is for the most part better to designate those salts by the name of the metal itself than by an adjective ending in *ic;* thus *potassium nitrate*, and *lead sulphate* are mostly to be preferred to *potassic nitrate* and *plumbic sulphate*. But in naming double salts, and in many cases where a numeral prefix is required, the names ending in *ic* are more euphonious; thus *triplumbic phosphate* sounds better than *trilead phosphate*, and *hydrodisodic phosphate* is certainly better than *hydrogen* and *disodium phosphate;* but there is no occasion for a rigid adherence to either system.

All oxygen-salts may also be represented as compounds of an acid oxide with one or more molecules of the same or different basic oxides, including water, *e. g.*:

Hydro-potassic sulphate	$2SO_4KH$	$= 2SO_3.K_2O.H_2O$
Sodio-tripotassic sulphate	$2(SO_4)_2KH$	$= 4SO_3.3K_2O.Na_2O$
Potassio-aluminic sulphate	$2(SO_4)_2Al'''K$	$= 4SO_3.Al'''_2O_3.K_2O$
Hydrodisodic phosphate	$2PO_4Na_2H$	$= P_2O_5.{}_2Na_2O.H_2O.$

When a normal oxygen-salt is thus formulated, it is easy to see that the number of molecules of acid oxide contained in its molecule is equal to the number of oxygen-atoms in the base; thus:

Normal potassium sulphate	SO_4K_2	$= SO_3.K_2O$
" barium sulphate	SO_4Ba	$= SO_3.BaO$
" stannic sulphate	$(SO_4)_2Sn''$	$= 2SO_3.SnO_2$
" aluminium sulphate	$(SO_4)_3Al'''_2$	$= 3SO_3.Al_2O_3.$

When the proportion of acid oxide is less than this, the salt is called *basic;* such salts may be regarded as compounds of a normal salt with one or more molecules of basic oxide, or as derived from normal salts by substitution of oxygen for an equivalent quantity of the acid radical; thus:

Tribasic lead nitrate .	$N_2O_5.3Pb''O$	$= (NO_3)_2Pb''.2Pb''O$
		$= Pb''_3(NO_3)_2O''_2$
Quadribasic aluminium sulphate	$3SO_3.4Al'''_2O_3$	$= (SO_4)_3Al'''_2.3Al'''_2O_3$
		$= Al'''_8(SO_4)''_3O''_9.$

The last mode of formulation exhibits the analogy of these basic oxysalts to the oxychlorides, oxyodides, &c.; thus the basic lead nitrate, $Pb_3(NO_3)2O_2$, just mentioned, is analogous to the oxychloride of that metal, $Pb_3Cl_2O_2$, which occurs native as mendipite.

The term basic and acid are sometimes applied to salts with reference to their action on vegetable colors. The normal salts formed by the union of the stronger acids with the alkalies and alkaline earths, such as potassium sulphate, SO_4K_2, barium nitrate, $(NO_3)_2Ba''$, &c., are perfectly neutral to vegetable colors, but most other normal salts exhibit either an acid or an alkaline reaction; thus ferrous sulphate, cupric sulphate, silver nitrate, and many others redden litmus, while the normal carbonates and phosphates of the alkali-metals exhibit a decided alkaline reaction. It is clear then that the action of a salt on vegetable colors bears no definite relation to its composition: hence the term *normal*, as applied to salts in which the basic hydro-

gen of the acid is wholly replaced, is preferable to *neutral*, and the terms *basic* and *acid*, as applied to salts, are best used in the manner above explained with reference to their composition.

When a normal salt containing a monoxide passes by oxidation to a salt containing a sesquioxide, dioxide, or trioxide, the quantity of acid present is no longer sufficient to saturate the base. Thus when a solution of ferrous sulphate, SO_4Fe, or $SO_3.FeO$ (common green vitriol), is exposed to the air, it absorbs oxygen, and an insoluble ferric salt is produced containing an excess of base, while normal ferric sulphate remains in solution:

$$\underset{\text{Ferrous sulphate.}}{4(SO_3.FeO)} + O_2 = \underset{\text{Normal ferric sulphate.}}{3SO_3.Fe_2O_3} + \underset{\text{Basic ferric sulphate.}}{SO_3.Fe_2O_3}$$

These basic salts are very often insoluble in water.

Salts containing a proportion of acid oxide larger than is sufficient to form a neutral compound, are called *anhydro-salts* (sometimes, though improperly, acid salts); they may evidently be regarded as compounds of a normal salt with excess of acid oxide; *e.g.:*

Sodium anhydrosulphate (bisulphate of soda) $\}$ $(SO_3)_2.Na_2O = (SO_4)Na_2.SO_3.$

Potassium anhydrochromate (bichromate of potash) $\}$ $(CrO_3)_2.K_2O = (CrO_4)K_2.CrO_3.$

The following is a list of the most important inorganic acids arranged according to their basicity:

Monobasic Acids.

Hydochloric	ClH	Antimonic	SbO_3H
Hydrobromic	BrH	Hypochlorous	$ClOH$
Hydriodic	IH	Chlorous	ClO_2H
Hydrofluoric	FH	Chloric	ClO_3H
Nitrous	NO_2H	Perchloric	ClO_4H
Nitric	NO_3H	Bromic	BrO_3H
Hypophosphorous	$(PH_2O_2)H$	Iodic	IO_3H
Metaphosphoric	PO_3H	Periodic	IO_4H
Boric	BO_2H		

Bibasic Acids.

Hydric (water)	OH_2	Selenious	SeO_3H_2
Sulph-hydric	SH_2	Selenic	SeO_4H_2
Selenhydric	SeH_2	Tellurous	TeO_3H_2
Tellurhydric	TeH_2	Telluric	TeO_4H_2
Sulphurous	SO_3H_2	Manganic	MnO_4H_2
Sulphuric	SO_4H_2	Permanganic	$Mn_2O_8H_2$
Hyposulphurous	$S_2O_3H_2$	Chromic	CrO_4H_2
Dithionic	$S_2O_6H_2$	Stannic	SnO_3H_2
Trithionic	$S_3O_6H_2$	Metasilicic	SiO_3H_2
Tetrathionic	$S_4O_6H_2$	Carbonic	CO_3H_2
Pentathionic	$S_5O_6H_2$	Phosphorous	$(PHO_3)H_2$

Tribasic Acids.

Orthophosphoric	PO_4H_3	Arsenic	AsO_4H_3

Tetrabasic Acids.

Pyrophosphoric	$P_2O_7H_4$	Orthosilicic	SiO_4H_4

The general characters of most of the non-metallic acids and their salts have been already considered; but the phosphates require further notice.

Phosphates. — There are three modifications of phosphoric acid: one being monobasic, the second tribasic, and the third tetrabasic, as indicated in the preceding table.

Hydrogen phosphide, PH_3, burnt in air or oxygen gas, takes up four atoms of oxygen, and forms *trihydric phosphate* or *tribasic phosphoric acid*, PO_4H_3. The same acid is produced by the oxidation of hypophosphorous or phosphorous acid; by oxidizing phosphorus with nitric acid (p. 214); by the decomposition of native calcium phosphate (apatite) and other native phosphates; and by the action of boiling water on phosphorus pentoxide, P_2O_5. This acid forms three distinct classes of metallic salts. With sodium, for example, it forms the three salts, PO_4NaH_2, PO_4Na_2H, and PO_4Na_3, the first two of which, still containing replaceable hydrogen, are acid salts, while the third is the normal or neutral salt.

If now the monosodic phosphate, PO_4NaH_2, be heated to redness, it gives off one molecule of water, and leaves an anhydrous monosodic phosphate, PO_3Na, the aqueous solution of which, when treated with lead nitrate, yields a lead-salt of corresponding composition; thus:

$$2PO_3Na + (NO_3)_2Pb'' = (PO_3)_2Pb'' + 2NO_3Na;$$

and this lead-salt decomposed by sulph-hydric acid, yields a monohydric acid having the composition PO_3H, possessing properties quite distinct from those of the trihydric acid above mentioned:

$$(PO_3)_2Pb'' + SH_2 = 2PO_3H + Pb''S.$$

The trihydric acid which is produced by the oxidation of phosphorus, and by the decomposition of the ordinary native phosphates, is called *orthophosphoric acid* or *ordinary phosphoric acid;* the monohydric acid is called *metaphosphoric acid.* The former may be regarded as a trihydrate, the latter as a monohydrate of phosphoric oxide:

$2PO_4H_3 = P_2O_5.3OH_2$, orthophosphoric acid,
$2PO_3H = P_2O_5.OH_2$, metaphosphoric acid.

Both are soluble in water, and the former may be produced by the action of boiling water, the latter by that of cold water on phosphoric oxide. They are easily distinguished from one another by their reactions with albumin and with silver nitrate. Metaphosphoric acid coagulates albumin, and gives a white precipitate with silver nitrate; whereas orthophosphoric acid does not coagulate albumin, and gives no precipitate, or a very slight one, with silver nitrate, till it is neutralized with an alkali, in which case a yellow precipitate is formed.

Metaphosphoric acid and its salts differ from orthophosphoric acid and the orthophosphates by the want of one or two atoms of water or base; thus:

Metaphosphates.		Orthophosphates.		
PO_3H	=	PO_4H_3	—	OH_2
PO_3Na	=	PO_4NaH_2	—	OH_2
$(PO_3)_2Ba''$	=	$(PO_4)_2Ba''H_4$	—	$2OH_2$
PO_3Ag	=	PO_4Ag_3	—	OAg_2
$(PO_3)_2Pb''$	=	$(PO_4)_2Pb''_3$	—	$2OPb''$.

Accordingly, we find that metaphosphates and orthophosphates are convertible one into the other by the loss or gain of one or two atoms of water or metallic base; thus:

α. A solution of metaphosphoric acid is converted, slowly at ordinary temperatures, quickly at the boiling heat, into orthophosphoric acid, and the metaphosphates of sodium and barium are converted by boiling with water into the corresponding monometallic orthophosphates (see the first three equations above). —*β*. The metaphosphate of a heavy metal, silver or lead, for example, is converted by boiling with water into a trimetallic phosphate and orthophosphoric acid:

$$3PO_3Ag + 3OH_2 = PO_4Ag_3 + 2PO_4H_3.$$

γ. When any metaphosphate is fused with an oxide, hydrate or carbonate, it becomes a trimetallic orthophosphate, *e. g.*;

$$PO_3Na + CO_3Na_2 = PO_4Na_3 + CO_2.$$

On the other hand (*δ*), when orthophosphoric acid is heated to redness, it loses water and becomes metaphosphoric acid; and when a monometallic orthophosphate is heated to redness, it also loses water and is transformed into a metaphosphate.

Intermediate between orthophosphates and metaphosphates, there are at least three distinct classes of salts, the most important of which are the *pyrophosphates* or *paraphosphates*, which may be derived from the tetrahydric or quadribasic acid, $P_2O_7H_4$, the normal sodium salt, for example, being $P_2O_7Na_4$, the normal lead salt, $P_2O_7Pb''_2$, &c. These salts may be viewed as compounds of orthophosphate and metaphosphate, *e. g.*:

$$P_2O_7Na_4 = PO_4Na_3 + PO_3Na.$$

Sodium pyrophosphate is produced by heating disodic orthophosphate to redness, a molecule of water being then given off:

$$2PO_4Na_2H = OH_2 + P_2O_7Na_4.$$

The aqueous solution of this salt yields insoluble pyrophosphates with lead and silver salts; thus with lead nitrate:

$$P_2O_7Na_4 + 2(NO_3)_2Pb'' = 4NO_3Na = P_2O_7Pb''_2,$$

and lead pyrophosphate decomposed by hydrogen sulphide yields hydrogen pyrophosphate or pyrophosphoric acid:

$$P_2O_7Pb''_2 + 2SH_2 = 2Pb''S + P_2O_7H_4.$$

Pyrophosphoric acid is distinguished from metaphosphoric acid by not coagulating albumin and not precipitating neutral solutions of barium or silver salts, and from orthophosphoric acid by producing a white instead of a yellow precipitate with silver nitrate.

Pyrophosphates are easily converted into metaphosphates and orthophosphates, and *vice versâ*, by addition or subtraction of water or a metallic base.

α. The production of a pyrophosphate from an orthophosphate by loss of water has been already mentioned. —*β*. Conversely, when a pyrophosphate is heated with water or a base, it becomes an orthophosphate, *e. g.*:

$$P_2O_7Na_4 + H_2O = 2PO_4Na_2H$$
$$P_2O_7Na_4 + 2ONaH = 2PO_4Na_3 + OH_2.$$

In like manner orthophosphoric acid heated to 215° is almost entirely converted into pyrophosphoric acid: $2PO_4H_3 - OH_2 = P_2O_7H_4$; and conversely, when pyrophosphoric acid is boiled with water, it is transformed into orthophosphoric acid.

γ. Pyrophosphoric acid heated to dull redness is converted into metaphosphoric acid: $P_2O_7H_4 - OH_2 = 2PO_3H$. The converse reaction is not

easily effected, inasmuch as metaphosphoric acid by absorbing water generally passes directly to the state of orthophosphoric acid. Peligot, however, observed the formation of pyrophosphoric from metaphosphoric acid by very slow absorption of water. — *δ.* When a metallic metaphosphate is treated with a proper proportion of a hydrate, oxide, or carbonate, it is converted into a pyrophosphate; thus:

$$\underset{\text{Metaphosphate.}}{2PO_3Na} + \underset{\text{Carbonate.}}{CO_3Na_2} = \underset{\text{Pyrophosphate.}}{P_2O_7Na_4} + \underset{\text{Carbon dioxide.}}{CO_2}$$

Fleitmann and Henneberg,* by fusing together a molecule of sodium pyrophosphate, $PO_4Na_3.PO_3Na$, with two molecules of metaphosphate, PO_3Na, obtained a salt having the composition $PO_4Na_3.3PO_3Na = P_4O_{13}Na_6$, which is soluble without decomposition in a small quantity of hot water, and crystallizes from its solution by evaporation over oil of vitriol. An excess of hot water decomposes it, but its cold aqueous solution is moderately permanent. Insoluble phosphates of similar composition may be obtained from the sodium-salt by double decomposition. Fleitmann and Henneberg obtained another crystallizable but very insoluble salt, having the composition $PO_4Na_3.9PO_3Na = P_{10}O_{31}Na_{12}$, by fusing together one molecule of sodium-pyrophosphate with eight molecules of the metaphosphate; and insoluble phosphates of similar constitution were obtained from it by double decomposition.

The comparative composition of these different phosphates is best shown by representing them as compounds of phosphoric oxide with metallic oxide, and assigning to them all, the quantity of base contained in the most complex member of the series; thus (for the sodium salts):

Orthophosphate	$2P_2O_5 . 6Na_2O = 4PO_4Na$
Pyrophosphate	$3P_2O_5 . 6Na_2O = 3P_2O_7Na_4$
Fleitmann and Henneberg's phosphate (*a*)	$4P_2O_5 . 6Na_2O = 2P_4O_{13}Na_6$
" " " " (*b*)	$5P_2O_5 . 6Na_2O = P_{10}O_{31}Na_{12}$
Metaphosphate	$6P_2O_5 . 6Na_2O = 12PO_3Na.$

Metallic Sulphides. — These compounds correspond, for the most part, to the oxides in composition: thus there are two sulphides of arsenic, As_2S_3 and As_2S_5, corresponding to the oxides, As_2O_3 and As_2O_5; also two sulphides of mercury, Hg_2S and HgS, analogous to the oxides, Hg_2O and HgO. Occasionally, however, we meet with oxides to which there are no corresponding sulphides (manganese dioxide, for example), and more frequently sulphides to which there are no corresponding oxides, the most remarkable of which are perhaps the alkaline polysulphides. Potassium, for example, forms the series of sulphides K_2S, K_2S_2, K_2S_3, K_2S_4, and K_2S_5, the third and fifth of which have no analogues in the oxygen series.

There are also sulph-hydrates analogous to the hydrates, and containing the elements of a metallic sulphide and hydrogen sulphide, or sulph-hydric acid; *e. g.* potassium sulph-hydrate $K_2S.H_2S = 2KHS$; lead sulph-hydrate $Pb''S.H_2S = Pb''H_2S_2$. Sulph-hydrates and sulphides may be derived from sulph-hydric acid by partial or total replacement of the hydrogen by metals, just as metallic hydrates and oxides are derived from water:

SHH	SKH	SKK
Sulph-hydric acid	Sulph-hydrate	Sulphide.
OHH	OKH	OKK
Water	Hydrate	Oxide.

* Ann. Ch. Pharm. lxv. 304.

Many metallic sulphides occur as natural minerals, especially the sulphides of lead, copper, and mercury, which afford valuable ores for the extraction of the metals, and iron bisulphide or iron pyrites, FeS_2, which is largely used as a source of sulphur, and for the preparation of ferrous sulphate.

Sulphides are formed artificially by heating metals with sulphur; by the action of metals on gaseous hydrogen sulphide; by the reduction of sulphates with hydrogen or charcoal; by heating metallic oxides in contact with gaseous hydrogen sulphide, or vapor of carbon bisulphide; and by precipitation of metallic solutions with hydrogen sulphide or a sulphide of alkali-metal. Some metals, as copper, lead, silver, bismuth, mercury, and cadmium, are precipitated from their acid solutions by hydrogen sulphide, passed into them as gas or added in aqueous solution, the sulphides of these metals being insoluble in dilute acids; others, as iron, cobalt, nickel, manganese, zinc, and uranium, form sulphides which are soluble in acids, and these are precipitated by hydrogen sulphide only from alkaline solutions, or by ammonium or potassium sulphide from neutral solutions. Many of these sulphides exhibit very characteristic colors, which serve as indications of the presence of the respective metals in solution (p. 201).

Metallic sulphides are also formed by the reduction of sulphates with organic substances; many native sulphides have doubtless been formed in this way.

The physical characters of some metallic sulphides closely resemble those of the metals in certain particulars, such as the peculiar opacity, lustre, and density, especially when they are in a crystalline condition. They are generally crystallizable, brittle, and of a gray, pale yellow, or dark brown color. The sulphides of the alkali-metals are soluble in water, most of the others are insoluble. They are frequently more fusible than the corresponding oxides, and some are volatilizable, as mercury sulphide and arsenic sulphide.

Many sulphides, when heated out of contact with atmospheric air, do not undergo any decomposition; this is the case chiefly with those containing the smallest proportions of sulphur, such as the monosulphides of iron and zinc. Sulphides containing larger proportions of sulphur are partially decomposed by heat, losing part of their sulphur, and being converted into lower sulphides; as in the case of iron bisulphide. The sulphides of gold and platinum are completely reduced by heat.

By the simultaneous action of heat and of substances capable of combining with sulphur, some sulphides may be decomposed. Thus, for instance, silver, copper, bismuth, tin, and antimony sulphides are reduced by hydrogen; copper, lead, mercury, and antimony sulphides are reduced by heating with iron.

Sulphides which are not reduced by heat alone, are always decomposed when heated in contact with oxygen or atmospheric air. Those of the alkali-metals and earth-metals are converted into sulphates by this means. Zinc, iron, manganese, copper, lead, and bismuth sulphides are converted into oxides, and sulphurous oxide is produced; but when the temperature is not above dull redness, some sulphate is formed by direct oxidation. Mercury and silver sulphides are completely reduced to the metallic state. Some native sulphides gradually undergo alteration by mere exposure to the atmosphere; but it is then generally limited to the production of sulphates, unless the oxidation takes place so rapidly that the heat generated is sufficient to decompose the sulphate first produced. In the production of some metals for use in the arts, the separation of sulphur from the native minerals is effected chiefly by means of this action in the operation of roasting.

Metallic sulphides are decomposed in like manner when heated with metallic oxides in suitable proportions, yielding sulphurous oxide and the

metal of both the sulphide and oxide. Lead is reduced from the native sulphide in this manner.

Many metallic sulphides are decomposed by acids in the presence of water, sulphuretted hydrogen being evolved while the metal enters into combination with the acid or chlorous radical of the acid. Nitric acid when concentrated decomposes most sulphides, with formation of metallic oxide, sulphuric acid, sulphur, and a lower oxide of nitrogen. Nitromuriatic acid acts in a similar manner, but still more energetically.

Sulphur-salts. — The sulphides of the more basylous metals unite with those of the more chlorous or electro-negative metals, and of the metalloïds, forming *sulphur-salts*, analogous in composition to the oxygen-salts, *e. g.:*

Carbonate	$CO_3K_2 = CO_2.K_2O$
Sulphocarbonate	$CS_3K_2 = CS_2.K_2S$
Arsenate	$2AsO_4K_3 = As_2O_5.3K_2O$
Sulpharsenate	$2AsS_4K_3 = As_2S_5.3K_2S$

Selenides and Tellurides. — These compounds are analogous in composition, and in many of their properties, to the sulphides, and likewise unite one with the other, forming selenium-salts and tellurium salts analogous to the oxygen and sulphur salts.

Metals also form definite compounds with nitrogen, phosphorus, silicon, boron, and carbon; but these compounds are comparatively unimportant, excepting the carbonides of iron, which form cast iron and steel.

CLASS I.—MONAD METALS.

GROUP I.—METALS OF THE ALKALIES.

POTASSIUM.

Atomic weight, 39·1. Symbol, K (Kalium).

POTASSIUM was discovered in 1807 by Sir H. Davy, who obtained it in very small quantity by exposing a piece of moistened potassium hydrate to the action of a powerful voltaic battery, the alkali being placed between a pair of platinum plates connected with the apparatus. Processes have since been devised for obtaining this metal in almost any quantity that can be desired.

An intimate mixture of potassium carbonate and charcoal is prepared by calcining, in a covered iron pot, the crude tartar of commerce; when cold it is rubbed to powder, mixed with one tenth part of charcoal in small lumps, and quickly transferred to a retort of stout hammered iron: the latter may be one of the iron bottles in which mercury is imported. The retort is introduced into a furnace *a* (fig. 162), and placed horizontally on supports of fire-brick, *f*, *f*. A wrought-iron tube *d*, four inches long, serves to convey the vapors of potassium into a receiver *e*, formed of two pieces of wrought-iron, *a*, *b* (fig. 163), which are fitted closely to each other so as to form a shallow box only a quarter of an inch deep, and are kept together by clamp-screws. The iron plate should be one sixth of an inch thick, twelve inches long, and five inches wide. The receiver is open at both ends, the socket fitting upon the neck of the iron bottle. The object of giving the receiver this flattened form is to ensure the rapid cooling of the potassium, and thus to withdraw it from the action of the carbon monoxide, which is disengaged during the entire process, and has a strong tendency to unite with the potassium, forming a dangerously explosive compound. Before connecting the receiver with the tube *d*, the fire is slowly raised till the iron bottle attains a dull red heat. Powdered vitrefied borax is then sprinkled upon it, which melts and forms a coating, serving to protect the iron from oxidation. The heat is then to be urged until it is very intense, care being taken to raise it as equally as possible throughout every part of the furnace. When a full reddish-white heat is attained, vapors of potassium begin to appear and burn with a bright flame. The receiver is then adjusted to the end of the tube, which must not project more than a quarter of an inch through the iron plate forming the front wall of the furnace; otherwise the tube is liable to be obstructed by the accumulation of solid potassium, or of the explosive compound above mentioned. Should any obstruction occur, it must be removed by thrusting in an iron bar, and if this fail, the fire must be immediately withdrawn by removing the bars from the furnace, with the exception of two which support the iron bottle. The receiver is kept cool by the application of a wet cloth to its outside. When the operation is complete, the receiver with the potassium is removed and immedi-

ately plunged into a vessel of rectified Persian naphtha provided with a cover, and kept cool by immersion in water. When the apparatus is sufficiently cooled, the potassium is detached and preserved under naphtha.

Fig. 162.

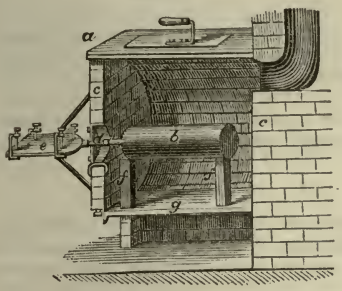
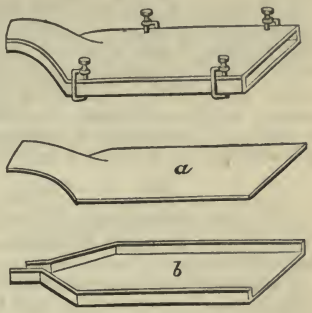


Fig. 163.



If the potassium be wanted absolutely pure, it must be afterwards redistilled in an iron retort, into which some naphtha has been put, that its vapor may expel the air, and prevent oxidation of the metal.

Potassium is a brilliant white metal, with a high degree of lustre; at the common temperature of the air it is soft, and may be easily cut with a knife, but at 0° it is brittle and crystalline. It melts completely at 62·5°, and distils at a low red heat. It floats on water, its specific gravity being only 0·865.

Exposed to the air, potassium oxidizes instantly, a tarnish covering the surface of the metal, which quickly thickens to a crust of caustic potash. Thrown upon water, it takes fire spontaneously, and burns with a beautiful purple flame, yielding an alkaline solution. When it is brought into contact with a little water in a jar standing over mercury, the liquid is decomposed with great energy, and hydrogen liberated. Potassium is always preserved under the surface of naphtha.

Potassium Chloride, KCl. — This salt is obtained in large quantity in the manufacture of the chlorate: it is easily purified from any portions of the latter by exposure to a dull red heat. Within the last few years large quantities of this salt have been obtained from sea-water, by a peculiar process suggested by M. Balard.* It is also contained in kelp, and is separated for the use of the alum-maker. Considerable quantities of it are now obtained from the salt-beds of Strassfurt, near Magdeburg, in Prussia.

Potassium chloride closely resembles common salt in appearance, assuming, like that substance, the cubic form of crystallization. The crystals dissolve in three parts of cold, and in a much smaller quantity of boiling water: they are anhydrous, have a simple saline taste, with slight bitterness, and fuse when exposed to a red heat. Potassium chloride is volatilized by a very high temperature.

Potassium Iodide, KI. — There are three different methods of preparing this important medicinal compound.

(1.) When iodine is added to a strong solution of caustic potash free from carbonate, it is dissolved in large quantity, forming a colorless solution containing potassium iodide and iodate; the reaction is the same as in the

* Reports by the Juries of the International Exhibition of 1862, Class II.

analogous case with chlorine. When the solution begins to be permanently colored by the iodine, it is evaporated to dryness, and cautiously heated to redness, by which the iodate is entirely converted into potassium iodide. The mass is then dissolved in water, and, after filtration, made to crystallize.

(2.) Iodine, water, and iron filings or scraps of zinc, are placed in a warm situation until the combination is complete, and the solution colorless. The resulting iodide of iron or zinc is then filtered, and exactly decomposed with solution of pure potassium carbonate, great care being taken to avoid excess of the latter. Potassium iodide and ferrous carbonate, or zinc carbonate, are thus obtained: the former is separated by filtration, and evaporated until the solution is sufficiently concentrated to crystallize on cooling, the washings of the filter being added to avoid loss:

$$FeI_2 + CO_3K_2 = 2KI + CO_3Fe''.$$

(3.) A very simple method for the preparation of potassium iodide has recently been proposed by Liebig. One part of amorphous phosphorus is added to 40 parts of warm water; 20 parts of dry iodine are then gradually added and intimately mixed with the phosphorus by trituration. The dark-brown liquid thus obtained is now heated on the water-bath until it becomes colorless; it is then poured off from the undissolved phosphorus and neutralized, first with barium carbonate and then with baryta water, until it becomes slightly alkaline. The insoluble barium phosphate is filtered off and washed; the filtrate now contains nothing but barium iodide, which, when treated with potassium sulphate, yields insoluble barium sulphate and potassium iodide in solution. Lime answers nearly as well as baryta.

Potassium iodide crystallizes in cubes, which are often, from some unexplained cause, milk-white and opaque: they are anhydrous, and fuse readily when heated. The salt is very soluble in water, but not deliquescent, when pure, in a moderately dry atmosphere: it is dissolved by alcohol.

Solution of potassium iodide, like those of all the soluble iodides, dissolves a large quantity of free iodine, forming a deep-brown liquid, not decomposed by water.

Potassium Bromide, KBr. — This compound may be obtained by processes exactly similar to those just described, substituting bromine for the iodine. It is a colorless and very soluble salt, quite undistinguishable in appearance and general characters from the iodide.

Potassium Oxides. — Potassium combines with oxygen in three proportions, forming a monoxide, OK_2, a dioxide, O_2K_2, and a tetroxide, O_4K_2, besides a hydrate, OKH, corresponding to the monoxide.

Potassium monoxide, OK_2, also called *anhydrous potash*, or *potassa*, is formed when potassium in thin slices is exposed at ordinary temperatures to dry air free from carbon dioxide; also when the hydrate is heated with an equivalent quantity of metallic potassium:

$$2OKH + K_2 = 2OK_2 + H_2.$$

It is white, very deliquescent and caustic. combines energetically with water, forming potassium hydrate, and becoming incandescent when moistened with it; melts at a red heat, and volatilizes at very high temperatures.

The *dioxide* O_2K_2 or $\begin{vmatrix} OK \\ OK \end{vmatrix}$ is formed at a certain stage in the preparation of the tetroxide, but has not been obtained quite pure. By carefully regulating the heat and supply of air, nearly the whole of the potassium

may be converted into a white oxide, having nearly the composition of the dioxide. An aqueous solution of this oxide is formed by the action of water on the tetroxide. The *tetroxide*, O_4K_2, or $\begin{matrix} O—O—K \\ | \\ O—O—K \end{matrix}$, is produced when potassium is burnt in excess of dry air or oxygen gas. It is a chrome-yellow powder, which cakes together at about 280°. It absorbs moisture rapidly, and is decomposed by water, giving off oxygen and forming a solution of the dioxide. When gently heated in a stream of carbon monoxide, it yields potassium carbonate and two atoms of oxygen:

$$O_4K_2 + CO = CO_3K_2 + O_2:$$

with carbon dioxide it acts in a similar manner, giving off three atoms of oxygen.*

Potassium Hydrate, OKH, commonly called *caustic potash*, or *potassa*, is a very important substance, and one of great practical utility. It is always prepared for use by decomposing the carbonate with calcium hydrate (slaked lime), as in the following process, which is very convenient: 10 parts of potassium carbonate are dissolved in 100 parts of water, and heated to ebullition in a clean untinned iron, or, still better, silver vessel; 8 parts of good quicklime are meanwhile slaked in a covered basin, and the resulting calcium hydrate added, little by little, to the boiling solution of carbonate, with frequent stirring. When all the lime has been introduced, the mixture is suffered to boil for a few minutes, and then removed from the fire and covered up. In the course of a very short time, the solution will have become quite clear, and fit for decantation, the calcium carbonate, with the excess of hydrate, settling down as a heavy, sandy precipitate. The solution should not effervesce with acids.

It is essential in this process that the solution of potassium carbonate be dilute, otherwise the decomposition becomes imperfect. The proportion of lime recommended is much greater than that required by theory, but it is always proper to have an excess.

The solution of potassium hydrate may be concentrated by quick evaporation in the iron or silver vessel to any desired extent; when heated until vapor of water ceases to be disengaged, and then suffered to cool, it furnishes the solid hydrate, OKH, or $OK_2.OH_2$.

Pure potassium hydrate is also easily obtained by heating to redness for half an hour in a covered copper vessel, one part of pure powdered nitre with two or three parts of finely divided copper foil. The mass, when cold, is treated with water.

Potassium hydrate is a white solid substance, very deliquescent and soluble in water; alcohol also dissolves it freely, which is the case with comparatively few potassium compounds: the solid hydrate of commerce, which is very impure, may thus be purified. The solution of this substance possesses, in the very highest degree, the properties termed alkaline: it restores the blue color to litmus which has been reddened by an acid; neutralizes completely the most powerful acids; has a nauseous and peculiar taste; and dissolves the skin, and many other organic matters, when the latter are subjected to its action. It is frequently used by surgeons as a cautery, being moulded into little sticks for that purpose.

Potassium hydrate, both in the solid state and in solution, rapidly absorbs carbonic acid from the air; hence it must be kept in closely stopped bottles. When imperfectly prepared, or partially altered by exposure, it effervesces with an acid.

* Harcourt, Chem. Soc. Journ. xiv. 267.

This compound is not decomposed by heat, but volatilizes undecomposed at a very high temperature.

The following table of the densities and value in anhydrous potassium oxide, OK_2, of different solutions of potassium hydrate, is given on the authority of Dalton:

Density.	Percentage of OK_2.	Density.	Percentage of OK_2.
1·68	51·2	1·33	26·3
1·60	46·7	1·28	23·4
1·52	42·9	1·23	19·5
1·47	39·6	1·19	16·2
1·44	36·8	1·15	13·0
1·42	34·4	1·11	9·5
1·39	32·4	1·06	4·7
1·36	29·4		

Potassium Nitrate; Nitre; Saltpetre, $NO_3K = NO_2(OK)$. — This important compound is a natural product, being disengaged by a kind of efflorescence from the surface of the soil in certain dry and hot countries. It may also be produced by artificial means — namely, by the oxidation of ammonia in presence of a powerful base.

In France, large quantities of artificial nitre are prepared by mixing animal refuse of all kinds with old mortar or calcium hydrate and earth, and placing the mixture in heaps, protected from the rain by a roof, but freely exposed to the air. From time to time the heaps are watered with putrid urine, and the mass turned over, to expose fresh surfaces to the air. When much salt has been formed, the mixture is lixiviated, and the solution, which contains calcium nitrate, is mixed with potassium carbonate; calcium carbonate is formed, and the nitric acid transferred to the alkali. The filtered solution is then made to crystallize, and the crystals are purified by re-solution and crystallization, the liquid being stirred to prevent the formation of large crystals.

The greater part of the nitre used in this country comes from the East Indies: it is dissolved in water, a little potassium carbonate added to precipitate lime, and then the salt purified as above.

Considerable quantities of nitre are now manufactured by decomposing native sodium nitrate (Chile saltpetre), with carbonate or chloride of potassium. In Belgium the potassium carbonate obtained from the ashes of the beetroot sugar manufactories is largely used for this purpose; the potassium nitrate thus prepared is very pure, and is produced at a low price.

Potassium nitrate crystallizes in anhydrous six-sided prisms, with dihedral summits, belonging to the rhombic or trimetric system: it is soluble in 7 parts of water at 15·5°, and in its own weight of boiling water. Its taste is saline and cooling, and it is without action on vegetable colors. At a temperature below redness it melts, and by a strong heat is completely decomposed.

When it is thrown on the surface of many metals in a state of fusion, or when mixed with combustible matter and heated, rapid oxidation ensues, at the expense of the oxygen of the nitric acid. Examples of such mixtures are found in common gunpowder, and in nearly all pyrotechnic compositions, which burn in this manner independently of the oxygen of the air, and even under water. Gunpowder is made by very intimately mixing together potassium nitrate, charcoal, and sulphur, in proportions which approach 2 molecules of nitre, 3 atoms of carbon, and 1 atom of sulphur.

These quantities give, reckoned to 100 parts, and compared with the proportions used in the manufacture of the English Government powder,* the following results:

* Dr. M'Culloch, Encyclopædia Britannica.

	Theory.	Proportions in practice.
Potassium nitrate	74·8	75
Charcoal	13·3	15
Sulphur	11·9	10
	100·0	100

The nitre is rendered very pure by the means already mentioned, freed from water by fusion, and ground to fine powder; the sulphur and charcoal, the latter being made from light wood, as dogwood or alder, are also finely ground, after which the materials are weighed out, moistened with water, and thoroughly mixed by grinding under an edge-mill. The mass is then subjected to great pressure, and the millcake thus produced broken in pieces, and placed in sieves made of perforated vellum, moved by machinery, each containing, in addition, a round piece of heavy wood. The grains of powder broken off by attrition fall through the holes in the skin, and are easily separated from the dust by sifting. The powder is, lastly, dried by exposure to steam-heat, and sometimes glazed or polished by agitation in a kind of cask mounted on an axis.

It was formerly supposed that when gunpowder is fired, the whole of the oxygen of the potassium nitrate was transferred to the carbon, forming carbon dioxide, the sulphur combining with the potassium, and the nitrogen being set free. There is no doubt that this reaction does take place to a considerable extent, and that the large volume of gas thus produced, and still further expanded by the very exalted temperature, sufficiently accounts for the explosive effects. But recent investigations by Bunsen, Karolyi, and others, have shown that the actual products of the combustion of gunpowder are much more complicated than this theory would indicate, a very large number of products being formed, and a considerable portion of the oxygen being transferred to the potassium sulphide, converting it into sulphate, which, in fact, constitutes the chief portion of the solid residue and of the smoke formed by the explosion.*

Potassium Chlorate, $ClO_3K = ClO_2(OK)$. — The theory of the production of chloric acid, by the action of chlorine gas on a solution of caustic potassa, has been already explained (p. 187).

Chlorine gas is conducted by a wide tube into a strong and warm solution of potassium carbonate, until absorption of the gas ceases; and the liquid is, if necessary, evaporated, and then allowed to cool, in order that the slightly soluble chlorate may crystallize out. The mother-liquor affords a second crop of crystals, but they are much more contaminated by potassium chloride. It may be purified by one or two re-crystallizations.

Potassium chlorate is soluble in about 20 parts of cold and 2 of boiling water: the crystals are anhydrous, flat, and tabular; in taste it somewhat resembles nitre. When heated, it gives off the whole of its oxygen gas and leaves potassium chloride. By arresting the decomposition when the evolution of gas begins to slacken, and redissolving the salt, potassium perchlorate and chloride may be obtained.

This salt deflagrates violently with combustible matter, explosion often occurring by friction or blows. When about one grain-weight of chlorate and an equal quantity of sulphur are rubbed in a mortar, the mixture explodes with a loud report: hence it cannot be used in the preparation of gunpowder instead of the nitrate. Potassium chlorate is now a large article of commerce, being employed, together with phosphorus, in making instantaneous-light matches.

Potassium Perchlorate, $ClO_4K = ClO_3(OK)$.—This salt has been already

* See Watts's Dictionary of Chemistry, vol. ii. p. 958.

noticed under the head of perchloric acid. It is best prepared by projecting powdered potassium chlorate into warm nitric acid, when the chloric acid is resolved into perchloric acid, chlorine and oxygen gases. The salt is separated by crystallization from the nitrate. Potassium perchlorate is a very slightly soluble salt: it requires 55 parts of cold water, but is more freely taken up at a boiling heat. The crystals are small, and have the figure of an octohedron with square base. It is decomposed by heat, in the same manner as the chlorate.

Potassium Carbonates. — Potassium forms two well-defined carbonates, namely, a normal or neutral carbonate, CO_3K_2, and an acid salt containing CO_3KH.

Normal potassium carbonate, or *dipotassic carbonate* $= CO(OK)_2 = CO_2.OK_2$. Potassium-salts of vegetable acids are of constant occurrence in plants, where they perform important, but not yet perfectly understood functions in the economy of those beings. The potassium is derived from the soil, which, when capable of supporting vegetable life, always contains that substance. When plants are burned, the organic acids are destroyed, and the potassium is left in the state of carbonate.

It is by these indirect means that the carbonate, and, in fact, nearly all the salts of potassium, are obtained. The great natural depository of the alkali is the felspar of granitic and other unstratified rocks, where it is combined with silica, and in an insoluble state. The extraction thence is attended with great difficulties, and many attempts at manufacturing it on a large scale from this source have failed; but experiments quite recently made by Mr. T. O. Ward appear to indicate that the object may be accomplished by fusing potassic rocks with a mixture of calcium carbonate and fluoride. There are, however, natural processes at work, by which the potash is constantly being eliminated from these rocks. Under the influence of atmospheric agencies, these rocks disintegrate into soils, and as the alkali acquires solubility, it is gradually taken up by plants, and accumulates in their substance in a condition highly favorable to its subsequent applications.

Potassium-salts are always most abundant in the green and tender parts of plants, as may be expected, since from these, evaporation of nearly pure water takes place to a large extent: the solid timber of forest-trees contains comparatively little.

In preparing the salt on an extensive scale, the ashes are subjected to a process called lixiviation: they are put into a large cask or tun, having an aperture near the bottom, stopped by a plug, and a quantity of water is added. After some hours the liquor is drawn off, and more water added, that the whole of the soluble matter may be removed. The weakest solutions are poured upon fresh quantities of ash, in place of water. The solutions are then evaporated to dryness, and the residue calcined, to remove a little brown organic matter: the product is the crude potash or pearlash of commerce, of which very large quantities are obtained from Russia and America. This salt is very impure: it contains potassium silicate, sulphate, chloride, &c.

The purified potassium carbonate of pharmacy is prepared from the crude article by adding an equal weight of cold water, agitating and filtering: most of the foreign salts are, from their inferior degree of solubility, left behind. The solution is then boiled down to a very small bulk, and suffered to cool, when the carbonate separates in small crystals containing 2 molecules of water, $CO_3K_2.2OH_2$; these are drained from the mother-liquor, and then dried in a stove.

A still purer salt may be obtained by exposing to a red-heat purified cream of tartar (acid potassium tartrate), and separating the carbonate by solution in water and crystallization, or evaporation to dryness.

Potassium carbonate is extremely deliquescent, and soluble in less than its own weight of water: the solution is highly alkaline to test-paper. It is insoluble in alcohol. By heat the water of crystallization is driven off, and by a temperature of full ignition the salt is fused, but not otherwise changed. This substance is largely used in the arts, and is a compound of great importance.

Acid potassium carbonate, *Hydrogen potassium carbonate*, or *Mono-potassic carbonate*, $CO_3KH = CO_2(KHO)$; commonly called *bicarbonate of potash*. — When a stream of carbonic acid gas is passed through a cold solution of potassium carbonate, the gas is rapidly absorbed, and a white, crystalline, and less soluble substance separated, which is the acid salt. It is collected, pressed, re-dissolved in warm water, and the solution left to crystallize.

Acid potassium carbonate is much less soluble than the normal carbonate: it requires for that purpose 4 parts of cold water. The solution is nearly neutral to test-paper, and has a much milder taste than the normal salt. When boiled it gives off carbon dioxide. The crystals, which are large and beautiful, derive their form from a monoclinic prism: they are decomposed by heat, water and carbon dioxide being evolved, and normal carbonate left behind:

$$2CO_3KH = CO_3K_2 + OH_2 + CO_2.$$

Potassium Sulphates. — Potassium forms a normal or neutral sulphate, two acid sulphates, and an anhydrosulphate.

Normal potassium sulphate, or *Bipotassic sulphate*, $SO_4K_2 = SO_2(OK)_2 = SO_3.OK_2$, is obtained by neutralizing the acid residue left in the retort when nitric acid is prepared, with crude potassium carbonate. The solution yields, on cooling, hard transparent crystals of the neutral sulphate, which may be re-dissolved in boiling water, and re-crystallized.

Potassium sulphate is soluble in about 10 parts of cold, and in a much smaller quantity of boiling water: it has a bitter taste, and is neutral to test-paper. The crystals are combinations of rhombic pyramids and prisms, much resembling those of quartz in figure and appearance: they are anhydrous, and decrepitate when suddenly heated, which is often the case with salts containing no water of crystallization. They are quite insoluble in alcohol.

Acid potassium sulphate, *Hydrogen and potassium sulphate*, or *Monopotassic sulphate*, $SO_4KH = SO_2(OK)(OH) = SO_3.OKH$, commonly called *bisulphate of potash*. — To obtain this salt, the neutral sulphate in powder is mixed with half its weight of oil of vitriol, and the whole evaporated quite to dryness in a platinum vessel, placed under a chimney: the fused salt is dissolved in hot water, and left to crystallize. The crystals have the figure of flattened rhombic prisms, and are much more soluble than the neutral salt, requiring only twice their weight of water at 15·5°, and less than half that quantity at 100°. The solution has a sour taste and strongly acid reaction.

Another *acid sulphate*, containing $(SO_4)_3K_4H_2$ or $2SO_4K_2.SO_4H_2$, crystallizing in fine needles resembling asbestos, was obtained by Phillips from the nitric acid residue. Jacquelain was unsuccessful in his attempts to reproduce this compound.

The *anhydrosulphate*, $SO_4K_2.SO_3 = 2SO_3.OK_2$, commonly called *anhydrous bisulphate of potash*, is obtained by dissolving equal weights of the normal sulphate and oil of vitriol in a small quantity of warm distilled water, and leaving the solution to cool. The anhydrous sulphate crystallizes out in long delicate needles, which if left for several days in the mother-liquor, disappear, and give place to crystals of the ordinary acid sulphate above described. This salt is decomposed by a large quantity of water.*

* Jacquelain, Ann. Chim. Phys. [3], vol. vii. p. 311.

Potassium Sulphides. — Potassium heated in sulphur vapor burns with great brilliancy. It unites with sulphur in five different proportions, forming the compounds SK_2, S_2K_2, S_3K_2, S_4K_2, S_5K_2; also a sulph-hydrate, SKH.

Monosulphide, SK_2. — It is doubtful whether this compound has been obtained in the pure state. It is commonly said to be produced by heating potassium sulphate in a current of dry hydrogen, or by igniting the same salt in a covered vessel with finely divided charcoal; but, according to Bauer, one of the higher sulphides is always formed at the same time, together with oxide of potassium. The product has a reddish-yellow color, is deliquescent, and acts as a caustic on the skin. When potassium sulphate is heated in a covered crucible with excess of lamp-black, a mixture of potassium sulphide and finely divided carbon is obtained, which takes fire spontaneously on coming in contact with the air. The monosulphide might perhaps be obtained pure by heating 1 molecule of potassium sulph-hydrate, KHS, with 1 atom of the metal.

When sulph-hydric acid gas is passed to saturation into a solution of caustic potash, a solution of the sulph-hydrate is obtained, which is colorless at first, but if exposed to the air, quickly absorbs oxygen, and turns yellow, in consequence of the formation of bisulphide:

$$2SKH + O = S_2K_2 + OH_2.$$

If a solution of potash be divided into two equal parts, and one half saturated with hydrogen sulphide, and then mixed with the other, a solution is formed which may contain potassium monosulphide:

$$SKH + OKH = SK_2 + OH_2.$$

But it is also possible that the hydrate and the sulph-hydrate may mix without mutual decomposition. The solution, when mixed with one of the stronger acids, gives off hydrogen sulphide without deposition of sulphur, a reaction which is consistent with either view of its constitution.

The *bisulphide*, S_2K_2, is formed, as already observed, on exposing a solution of the sulph-hydrate to the air till it begins to show turbidity. By evaporation in a vacuum, it is obtained as an orange-colored, easily fusible substance.

The *trisulphide*, S_3K_2, is obtained by passing the vapor of carbon bisulphide over ignited potassium carbonate, as long as gas continues to escape:

$$2CO_3K_2 + 3CS_2 = 2S_3K_2 + 4CO + CO_2.$$

Also, together with potassium sulphate, forming one of the mixtures called *liver of sulphur*, by melting 552 parts (4 molecules) of potassium carbonate with 320 parts (10 atoms) of sulphur:

$$4CO_3K_2 + S_{10} = SO_4K_2 + 3S_3K_2 + 4CO_2.$$

The *tetrasulphide*, S_4K_2, is formed by reducing potassium sulphate with the vapor of carbon bisulphide.

The *pentasulphide*, S_5K_2, is formed by boiling a solution of any of the preceding sulphides with excess of sulphur till it is saturated, or by fusing either of them in the dry state with sulphur. The excess of sulphur then separates and floats above the dark-brown pentasulphide.

Liver of sulphur, or *hepar sulphuris*, is a name given to a brownish substance, sometimes used in medicine, made by fusing together different proportions of potassium carbonate and sulphur. It is a variable mixture of the two higher sulphides with hyposulphite and sulphate of potassium.

When equal parts of sulphur and dry potassium carbonate are melted together at a temperature not exceeding 250° C. (482° F.), the decomposi-

tion of the salt is quite complete, and all the carbon dioxide is expelled. The fused mass dissolves in water, with the exception of a little mechanically mixed sulphur, with dark-brown color, and the solution is found to contain nothing besides pentasulphide and hyposulphite of potassium:

$$3OK_2 + S_{12} = 2S_5K_2 + S_2O_3K_2.$$

When the mixture has been exposed to a temperature approaching that of ignition, it is found, on the contrary, to contain potassium sulphate, arising from the decomposition of the hyposulphite which then occurs:

$$4S_2O_3K_2 = S_5K_2 + 3SO_4K_2.$$

From both these mixtures the potassium pentasulphide may be extracted by alcohol, in which it dissolves.

When the carbonate is fused with half its weight of sulphur only, the trisulphide is produced, as above indicated, instead of the pentasulphide.

The effects described happen in the same manner when potassium hydrate is substituted for the carbonate; also, when a solution of the hydrate is boiled with sulphur, a mixture of sulphide and hyposulphite always results.

Potassium-salts are colorless, when not associated with a colored metallic oxide or acid. They are all more or less soluble in water, and may be distinguished by the following characters:

(1.) Solution of *tartaric acid*, added in excess to a moderately strong solution of potassium-salt, gives, after some time, a white crystalline precipitate of cream of tartar; the effect is greatly promoted by strong agitation.

(2.) Solution of *platinic chloride* with a little hydrochloric acid, if necessary, gives, under similar circumstances, a crystalline yellow precipitate, which is a double salt of platinum tetrachloride and potassium chloride. Both this compound and cream of tartar are, however, soluble in about 60 parts of cold water. An addition of alcohol increases the delicacy of both tests.

(3.) *Perchloric acid*, and *silicofluoric acid*, give rise to slightly soluble white precipitates when added to a potassium-salt.

(4.) Potassium-salts usually color the outer blowpipe-flame purple or violet: this reaction is clearly perceptible only when the potassium-salts are pure.

(5.) The spectral phenomena exhibited by potassium compounds are mentioned at p. 88.

SODIUM.

Atomic weight, 23. Symbol, Na. (Natrium).

Sodium is a very abundant element, and very widely diffused. It occurs in large quantities as chloride, in rock-salt, sea-water, salt-springs, and many other mineral waters; more rarely as carbonate, borate, and sulphate, in solution or in the solid state, and as silicate in many minerals.

Metallic sodium was obtained by Davy soon after the discovery of potassium, and by similar means. Gay-Lussac and Thénard afterwards prepared it by decomposing sodium hydrate with metallic iron at a white heat; and Brunner showed that it may be prepared with much greater facility by distilling a mixture of sodium carbonate and charcoal.

The preparation of sodium by this last-mentioned process is much easier than that of potassium, not being complicated, or only to a slight extent,

by the formation of secondary products. Within the last few years it has been considerably improved by Deville and others, and carried out on the manufacturing scale, sodium being now employed in considerable quantity as a reducing agent, especially in the manufacture of aluminium and magnesium, and in the silver amalgamation process.

The sodium carbonate used for the preparation is prepared by calcining the crystallized neutral carbonate. It must be thoroughly dried, then pounded and mixed with a slight excess of pounded charcoal or coal. An inactive substance, viz. pounded chalk, is also added to keep the mixture in a pasty condition during the operation, and prevent the fused sodium carbonate from separating from the charcoal. The following are the proportions recommended by Deville:

For Laboratory Operations.		*For Manufacturing Operations.*	
Dry sodium carbonate,	717 parts	Dry sodium carbonate,	30 kilogr.
Charcoal	175 "	Coal	13 "
Chalk	108 "	Chalk	3 "

These materials must be very intimately mixed by pounding and sifting, and it is advantageous to calcine the mixture before introducing it into the distilling apparatus, provided the calcination can be effected by the waste heat of a furnace; the mixture is thereby rendered more compact, so that a much larger quantity can be introduced into a vessel of given size.

The distillation is performed, on the laboratory scale, in a mercury bottle heated exactly in the manner described for the preparation of potassium. For manufacturing operations, the mixture is introduced into iron cylinders, which are heated in a reverberatory furnace, and so arranged that, at the end of the distillation, the exhausted charge may be withdrawn and a fresh charge introduced, without displacing the cylinders or putting out the fire. The receivers used in either case are the same in form and dimensions as those employed in the preparation of potassium (p. 291).

When the process goes on well, the sodium collected in the receivers is nearly pure; it may be completely purified by melting it under a thin layer of naphtha. This liquid is decanted as soon as the sodium becomes perfectly fluid, and the metal is run into moulds like those used for casting lead or zinc.

Sodium Chloride; Common Salt, NaCl. — This very important substance is found in many parts of the world in solid beds or irregular strata of immense thickness, as in Cheshire, Spain, Galicia, and many other localities. An inexhaustible supply exists also in the waters of the ocean, and large quantities are obtained from saline springs.

Rock-salt is almost always too impure for use. If no natural brine-spring exists, an artificial one is formed by sinking a shaft into the rock-salt, and, if necessary, introducing water. This when saturated is pumped up, and evaporated more or less rapidly in large iron pans. As the salt separates, it is removed from the bottom of the vessel by means of a scoop, pressed while still moist into moulds, and then transferred to the drying-stove. When large crystals are required, as for the coarse-grained *bay-salt* used in curing provisions, the evaporation is slowly conducted. Common salt is apt to be contaminated with magnesium chloride.

Sodium chloride, when pure, is not deliquescent in moderately dry air. It crystallizes in anhydrous cubes, which are often grouped together into pyramids, or steps. It requires about $2\frac{1}{2}$ parts of water at 15·5° C. (60° F.) for solution, and its solubility is not sensibly increased by heat; it dissolves to some extent in spirit of wine, but is nearly insoluble in absolute alcohol. It melts at a red heat, and is volatile at a still higher temperature. The economical uses of common salt are well known.

The *iodide and bromide of sodium* much resemble the corresponding potassium-compounds: they crystallize in cubes which are anhydrous, and very soluble in water.

Sodium Oxides. — Sodium forms a monoxide and a dioxide; also a hydrate corresponding to the former.

Sodium Monoxide, or *Anhydrous Soda*, ONa_2, is produced, together with the dioxide, when sodium burns in the air, and may be obtained pure by exposing the dioxide to a very high temperature; or by heating sodium hydrate with an equivalent quantity of sodium: $2ONaH + Na_2 = 2ONa_2 + H_2$. It is a gray mass, which melts at a red heat, and volatilizes with difficulty.

Sodium Hydrate, or *Caustic Soda*, ONaH or ONa_2, OH_2. — This substance is prepared by decomposing a somewhat dilute solution of sodium carbonate with calcium hydrate: the description of the process employed in the case of potassium hydrate, and the precautions necessary, apply word for word to that of sodium hydrate.

The solid hydrate is a white, fusible substance, very similar in properties to potassium hydrate. It is deliquescent, but dries up again after a time in consequence of the absorption of carbonic acid. The solution is highly alkaline, and a powerful solvent for animal matter: it is used in large quantity for making soap.

The strength of a solution of caustic soda may be roughly determined from a knowledge of its density, by the aid of the following table drawn up by Dalton:

TABLE OF PERCENTAGE OF ANHYDROUS SODA, ONa_2, IN SOLUTIONS OF DIFFERENT DENSITY.

Density.	Percentage of anhydrous soda.	Density.	Percentage of anhydrous soda.
2·00	77·8	1·40	29·0
1·85	63·6	1·36	26·0
1·72	53·8	1·32	23·0
1·63	46·6	1·29	19·0
1·55	41·2	1·23	16·0
1·50	36·8	1·18	13·0
1·47	34·0	1·12	9·0
1·44	31·0	1·06	4·7

Sodium Dioxide, O_2Na_2. — Sodium, when heated to about 200° in a current of dry air, absorbs oxygen, and is converted into dioxide: this substance is white, but becomes yellow when heated, which tint it again loses on cooling. It is soluble in water without decomposition: the solution may be evaporated under the receiver of the air-pump, and, when sufficiently concentrated, deposits crystalline plates having the composition $O_2Na_2.8OH_2$. These crystals left to effloresce over oil of vitriol for nine days lose three fourths of their water, and yield another hydrate containing $O_2Na_2.2OH_2$ (Harcourt). The aqueous solution of sodium dioxide when heated on the water-bath, is decomposed into oxygen and the monoxide.

Sodium Carbonates. — The *Neutral* or *Disodic Carbonate*, $CO_3Na_2.10OH_2$, was once exclusively obtained from the ashes of sea-weeds, and of plants, such as the *Salsola soda*, which grow by the sea-side, or, being cultivated in suitable localities for the purpose, are afterwards subjected to incineration. The *barilla*, still employed to a small extent in soap-making, is thus produced in several places on the coast of Spain, as Alicante, Carthagena, &c. That made in Brittany is called *varec*.

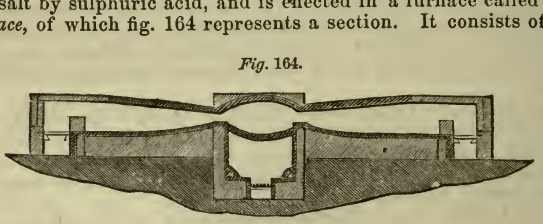
Sodium carbonate is now manufactured on a stupendous scale from common salt by a series of processes which may be divided into two stages: —

(1.) Manufacture of sodium sulphate, or salt-cake, from sodium chloride (common salt); this is called the salt-cake process.

(2.) Manufacture of sodium carbonate, or soda-ash; called the soda-ash process.

(1.) *Salt-cake process.* — This process consists in the decomposition of common salt by sulphuric acid, and is effected in a furnace called the *Salt-cake furnace*, of which fig. 164 represents a section. It consists of a large

Fig. 164.



covered iron pan, placed in the centre, and heated by a fire underneath; and two roasters, or reverberatory furnaces, placed one at each end, and on the hearths of which the salt is completely decomposed. The charge of half a ton of salt is first placed in the iron pan, and then the requisite quantity of sulphuric acid is allowed to pass in upon it. Hydrochloric acid is evolved, and escapes through a flue, with the products of combustion, into towers or scrubbers, filled with coke and bricks moistened with a stream of water; the whole of the acid vapors are thus condensed, and the smoke and heated air pass up the chimney. After the mixture of salt and acid has been heated in the iron pan, it becomes converted into a solid mass of acid sodium sulphate and undecomposed sodium chloride:

$$2NaCl + SO_4H_2 = NaCl + SO_4NaH + HCl.$$

It is then raked on to the hearths of the furnaces at each side of the decomposing pan, where the flame and heated air of the fire complete the decomposition into neutral sodium sulphate and muriatic acid:

$$NaCl + SO_4NaH = SO_4Na_2 + HCl.$$

(2.) *Soda-ash process.* — The sulphate is next reduced to powder, and mixed with an equal weight of chalk or limestone, and half as much small coal, both ground or crushed. The mixture is thrown into a reverberatory furnace, and heated to fusion, with constant stirring, 2 cwts. are about the quantity operated on at once. When the decomposition is judged complete, the melted matter is raked from the furnace into an iron trough, where it is allowed to cool. This crude product, called *black ash* or *ball-soda*, is broken up into little pieces, when cold, and lixiviated with cold or tepid water. The solution is evaporated to dryness, and the salt calcined with a little sawdust in a suitable furnace. The product is the *soda-ash*, or *British alkali* of commerce, which, when of good quality, contains from 48 to 52 per cent. of anhydrous soda, ONa_2, partly in the state of carbonate, and partly as hydrate, the remainder being chiefly sodium sulphate and common salt, with occasional traces of sulphite or hyposulphite, and also cyanide of sodium. By dissolving soda-ash in hot water, filtering the solution, and then allowing it to cool slowly, the carbonate is deposited in large transparent crystals.

The reaction which takes place in the calcination of the sulphate with chalk and coal-dust seems to consist, first, in the conversion of the sodium sulphate into sulphide by the aid of the combustible matter, and, secondly,

in the interchange of elements between that substance and the calcium carbonate:

SNa_2	+	CO_3Ca	=	SCa	+	CO_3Na_2
Sodium sulphide.		Calcium carbonate.		Calcium sulphide.		Sodium carbonate.

Other processes have been proposed, and even carried into execution; but the above, which was originally proposed by Leblanc, is found most advantageous.

The ordinary crystals of sodium carbonate contain ten molecules of water; but by particular management the same salt may be obtained with fifteen, nine, seven, molecules, or sometimes with only one. The common form of the crystals is derived from an oblique rhombic prism; they effloresce in dry air, and crumble to a white powder. Heated, they fuse in their water of crystallization; when the latter has been expelled, and the dry salt exposed to a full red heat, it melts without undergoing change. The common crystals dissolve in two parts of cold, and in less than their own weight of boiling water: the solution has a strong, disagreeable, alkaline taste, and a powerfully alkaline reaction.

Hydrogen and *Sodium Carbonate*, *Hydrosodic Carbonate*, *Monosodic Carbonate*, *Acid Sodium Carbonate*, CO_3NaH, or $CO_3Na_2.CO_3H_2$, commonly called *Bicarbonate of soda.* — This salt is prepared by passing carbonic acid gas into a cold solution of the neutral carbonate, or by placing the crystals in an atmosphere of the gas, which is rapidly absorbed, while the crystals lose the greater part of their water, and pass into the new compound.

Monosodic carbonate, prepared by either process, is a crystalline white powder, which cannot be re-dissolved in warm water without partial decomposition. It requires 10 parts of water at 15·5° for solution: the liquid is feebly alkaline to test-paper, and has a much milder taste than that of the simple carbonate. It does not precipitate a solution of magnesia. By exposure to heat, the salt is converted into neutral carbonate.

Dihydro-tetrasodic Carbonate, $(CO_3)_3Na_4H_2.2OH_2$. — This salt, commonly called *sesquicarbonate of soda*, may be regarded as a compound of the neutral and acid salts just described ($CO_3Na_2.2CO_3NaH$). It occurs native on the banks of the soda lakes of Sokenna, near Fezzan, in Africa, where it is called *trona;* also as *urao*, at the bottom of a lake in Maracaibo, South America. It is produced artificially, though with some difficulty, by mixing the monosodic and disodic carbonates in the proportions above indicated, melting them together, drying and exposing the dried mass in a cellar for some weeks; it then absorbs water, becomes crystalline, and contains spaces filled with the tetrasodic carbonate.

Sodium and *Potassium Carbonate*, $CO_3NaK.6OH_2$, separates in monoclinic crystals from a solution containing the two carbonates in equivalent proportions.

A mixture of these two carbonates in equivalent proportions melts at a much lower heat than either of the salts separately; such a mixture is very useful in the fusion of silicates, &c.

Alkalimetry. — Analysis of Alkaline Hydrates and Carbonates.

The amount of alkali or alkaline carbonate in commercial potash, soda, or ammonia, is estimated by determining the quantity of an acid of given strength required to neutralize a given weight of the sample. The estimation depends upon the facts that the alkaline salts of strong acids (sulphuric, oxalic, &c.) are neutral to litmus; and that the violet solution of litmus is colored blue by caustic alkalies or alkaline carbonates, wine-red by carbonic acid, and light red by strong acids.

The first step is the preparation of the standard acid. It is best to make this liquid of such strength that 1000 cubic centimetres (1 litre) shall contain exactly one ½ *gram-molecule* (*i. e.*, 1 molecule expressed in ½ grams) of the acid.

About 70 grams of concentrated sulphuric acid are diluted with about 600 grams of water; when the mixture is cool, the volume of it necessary to saturate 5·3 grams (one ½-decigram-molecule) of pure anhydrous sodium carbonate, CO_3Na_2, is determined.* For this purpose 5·3 grams of freshly ignited sodium carbonate are dissolved in hot water, the solution colored blue with a few drops of litmus, and the acid added from a burette or alkalimeter (p. 305), at last drop by drop, till the color just passes from wine-red to light red, and till strips of litmus-paper, moistened with the solution begin to retain the color when dry. The volume of acid employed is then noted, and the whole diluted so as to approximate to the required strength. Suppose, for instance, 37 cubic centimetres of acid have been used; water is then added till every 100 volumes is diluted to 250 volumes, and another determination is made. If 90 cubic centimetres are now required to saturate the ½-decigram alkaline solution, every 90 volumes of the acid must be diluted to 100, and the result controlled by a fresh determination; 100 cubic centimetres of this acid should exactly saturate 5·3 grams of sodium carbonate, and will contain 1 half-decigram-molecule of acid; 2 cubic centimetres will therefore contain 1 milligram-molecule (0·098 gram)† and will saturate 2 milligram-molecules of an alkali (OKH or ONaH), or 1 milligram-molecule of an alkaline carbonate (CO_3K_2 or CO_3Na_2).

To estimate the proportion of alkali in a commercial sample, a weighed portion of the substance is dissolved in water (if a solid), a few drops of litmus added, and the standard acid added from a burette, until the first permanent appearance of a light red color; and the volume of acid employed is read off. Each cubic centimetre of acid corresponds to 1 milligram-molecule of alkali, or 1 half milligram-molecule of alkaline carbonate; *i. e.*, to 0·053 gram sodium carbonate, CO_3Na_2, 0·069 gram potassium carbonate, CO_3K_2, 0.040 gram caustic soda ONaH, 0·056 gram caustic potash OKH, and 0·017 gram ammonia NH_3; and a simple proportion gives the amount of alkali or alkaline carbonate present (*e. g.* 100 : 6·9 : : number of cubic centimetres employed: potassium carbonate present). By operating on 100 times the ½-milligram-molecule (*e. g.* 6·9 grams in the case of potassium carbonate, 5·3 grams in the case of sodium carbonate), all calculation is saved: for as this amount, if present, would require 100 cubic centimetres of acid for its saturation, the number of cubic centimetres actually required at once indicates the percentage of alkaline carbonate. The burettes commonly used contain 50 cubic centimetres, and are graduated into half cubic centimeters; so that by operating on 50 times the ½-milligram-molecule, the number of divisions employed indicates the percentage.

Sometimes, instead of exactly neutralizing the alkali with the standard acid, it is better to add the acid till the litmus assumes a distinct light-red color, then heat the solution to boiling, and add a small excess (5 to 10 cubic centimetres) of acid. The hot solution is freed from carbonic acid by agitation and by drawing air through it with a glass tube; and then neutralized with a standard solution of caustic soda (100 cubic centimetres of which exactly saturate 100 cubic centimetres of the standard acid) till the color just changes from red to blue. Since the acid and alkaline solutions neutralize each other volume for volume, it is only necessary to deduct the number of cubic centimetres employed of the latter from that of the former, and calculate the amount of alkali from the residue. This method, called the *indirect* or *residual method*, is preferable to the direct method previously

* The molecule of sodium carbonate CO_3Na_2 weighs $12 + 48 + 46 = 106$.

† The molecular weight of sulphuric acid SO_4H_2 is $98 = 32 + 64 + 2$.

described, for the analysis of carbonates, since the change from blue to red is more distinctly marked than that from one shade of red to another.

The standard solution of caustic soda must be kept in a flask, into the cork of which is inserted a calcium chloride tube filled with a mixture of sodium sulphate and quicklime, which effectually prevents the absorption of carbonic acid. If the burette be closed with a similar tube, the soda solution may remain in it for days.

The "alkalimeter" or "burette" is a glass tube (fig. 165) closed at one end, and moulded into a spout or lip at the other, and marked with any convenient scale of equal parts, generally, as above mentioned, into 100 half cubic centimetres.* A strip of paper is pasted on the tube and suffered to dry, after which the instrument is graduated by counterpoising it in a nearly upright position in the pan of a balance of moderate delicacy and weighing into it, in succession, 5, 10, 15, 20, &c., grams of distilled water at 4° C. (39·2 F.) until the whole quantity, amounting to 50 grams (50 cubic centimetres), has been introduced, the level of the water in the tube being, after each addition, carefully marked with a pen upon the strip of paper, while the tube is held quite upright, and the mark made between the top and bottom of the curve formed by the surface of the water. The smaller divisions of the scale, of a half cubic centimetre each, may then be made by dividing with compasses each of the spaces into 10 equal parts. When the graduation is complete, and the operator is satisfied with its accuracy, the marks may be transferred to the tube itself by a sharp file, and the paper removed by a little warm water. The numbers are scratched on the glass with the hard end of the same file, or with a diamond. Or the glass is covered with etching wax, the scale traced upon it with a fine needle point, and the marks etched by exposing the tube to the vapor of hydrofluoric acid.

Fig. 165.

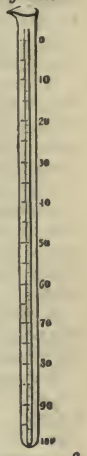
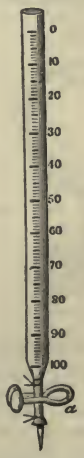


Fig. 166.

Fig. 167.

Fig. 168.



* It may also be divided into 1000 grain-measures, the grain-measure being the capacity of a grain of distilled water at 60° F.; 70,000 such measures go to an imperial gallon, and 8,750 to a pint.

The alkalimeter, represented in fig. 165, is the simplest form of this instrument. The pouring out of minute quantities is, however, greatly facilitated by providing the measure with a narrow dropping tube, fig. 166, the lower extremity of which is soldered into the measure, while the upper one is bent outward and sharply cut off. This kind of burette, which is known as Gay-Lussac's, is chiefly used in France. The liquid may be very conveniently poured from it; but it is rather easily broken, so that its manipulation requires a good deal of care. This defect is greatly obviated in the burette, fig. 167, in which the graduated tube is provided with a spout at the top, there being at the same time an orifice for pouring in the liquid.

A very elegant instrument has been contrived by Dr. Mohr of Coblentz. It is a graduated tube, drawn out at one end to a point, to which is attached, by means of a narrow vulcanized caoutchouc tube, a short glass tube, likewise drawn out to a point (fig. 168). There is a small space (about ¼ inch) between the two tubes, upon which is fixed a metallic clamp, *a*, represented in its actual dimensions in fig. 169. This clamp shuts off the connection between the graduated cylinder and the small glass tube. But by pressing with the fingers upon the ends, *b b*, of this clamp, it opens, and allows the liquid to flow out of the lower tube. It is evident that by this arrangement the amount of liquid may be regulated with the greatest nicety.

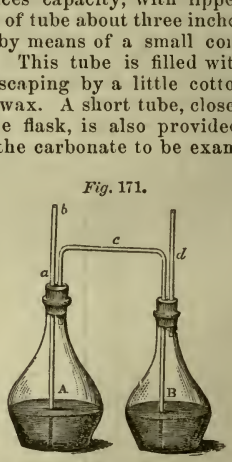
It is often desirable, in the analysis of carbonates, to determine directly the proportion of carbonic acid: the following methods leave nothing to be desired in point of precision:

A small light glass flask of three or four ounces capacity, with lipped edge, is chosen, and a cork fitted to it. A piece of tube about three inches long is drawn out at one extremity, and fitted, by means of a small cork and a bit of bent tube, to the cork of the flask. This tube is filled with fragments of calcium chloride, prevented from escaping by a little cotton at either end: the joints are secured by sealing-wax. A short tube, closed at one extremity, and small enough to go into the flask, is also provided, and the apparatus is complete. Fifty grains of the carbonate to be exam-

Fig. 169.

Fig. 170.

Fig. 171.



ined are carefully weighed out and introduced into the flask, together with a little water; the small tube is then filled with oil of vitriol, and placed in the flask in a nearly upright position, and leaning against its side in such a manner that the acid does not escape. The cork and calcium chloride tube are then adjusted, and the whole apparatus accurately counterpoised on the balance This done, the flask is slightly inclined, so that the oil of vitriol may slowly mix with the other substances and decompose the carbonate, the gas from which escapes in a dry state from the extremity

of the tube. When the action has entirely ceased, the liquid is heated until it boils, and the steam begins to condense in the drying-tube; it is then left to cool, and weighed, when the loss indicates the quantity of carbon dioxide. The acid must be in excess after the experiment. When calcium carbonate is thus analyzed, hydrochloric acid must be substituted for the sulphuric acid.

Instead of the above apparatus, a neat arrangement may be used, which was first suggested by Will and Fresenius. It consists of two small glass flasks, A and B, the latter being somewhat smaller than the former. Each of the flasks is provided with a doubly perforated cork. A tube, open at both ends, but closed at the upper extremity by means of a small quantity of wax, passes through the cork of A to the very bottom of the flask, whilst a second tube, reaching to the bottom of B, establishes a communication between the two flasks. The cork of B is provided, moreover, with a short tube *d*. In order to analyze a carbonate, a suitable quantity (fifty grains) is put into A, together with some water. B is half filled with concentrated sulphuric acid, the apparatus tightly fitted and weighed. A small quantity of air is now sucked out of flask B by means of the tube *d*, whereby the air in A is likewise rarefied. On allowing the air to return, a quantity of the sulphuric acid ascends to the tube *c*, and flows over into flask A, causing a disengagement of carbon dioxide, which escapes at *d*, after having been perfectly dried by passing through the bottle B. This operation is repeated until the whole of the carbonate is decomposed, and the process terminated by opening the wax stopper, and drawing a quantity of air through the apparatus. The apparatus is now re-weighed. The difference of the two weighings expresses the quantity of carbon dioxide in the compound analyzed.

Sodium Sulphate, $SO_4Na_2.10OH_2$, commonly called *Glauber's salt*, is a by-product in several chemical operations and an intermediate product in the manufacture of the carbonate as above described: it may of course be prepared directly, if wanted pure, by adding dilute sulphuric acid, to saturation, to a solution of sodium carbonate. It crystallizes in forms derived from an oblique rhombic prism: the crystals contain 10 molecules of water, are efflorescent, and undergo watery fusion when heated, like those of the carbonate: they are soluble in twice their weight of cold water, and rapidly increase in solubility as the temperature of the liquid rises to 33° C. (91·5° F), when a maximum is reached, 100 parts of water dissolving 117·9 parts of the salt, corresponding to 52 parts anhydrous sodium sulphate. When the salt is heated beyond this point, the solubility diminishes, and a portion of sulphate is deposited. A warm saturated solution, evaporated at a high temperature, deposits opaque prismatic crystals, which are anhydrous. The salt has a slightly bitter taste, and is purgative. Mineral springs sometimes contain it, as that at Cheltenham.

Sodium and Hydrogen Sulphate, or *Acid Sodium Sulphate*, $2SO_4NaH.3OH_2$, or $SO_4Na_2\,SO_4H_2.3OH_2$, commonly called *bisulphate of soda*, is prepared by adding to 10 parts of the anhydrous neutral sulphate, 7 of oil of vitriol, evaporating the whole to dryness, and gently igniting. The acid sulphate is very soluble in water, and has an acid reaction. It is not deliquescent. When very strongly heated, the fused salt gives up anhydrous sulphuric acid, and becomes neutral sulphate; a change which necessarily supposes the previous formation of an anhydro-bisulphate, $SO_4Na_2.SO_3$.

Sodium Hyposulphite, $S_2O_3Na_2$. — There are several modes of procuring this salt, which is now used in considerable quantity for photographic purposes and as antichlore. One of the best is to form neutral *sodium sulphite*, by passing a stream of well-washed sulphurous oxide gas into a

strong solution of sodium carbonate, and then digest the solution with sulphur at a gentle heat during several days. By careful evaporation at a moderate temperature, the salt is obtained in large and regular crystals, which are very soluble in water.

Sodium Nitrate, NO_3Na. — This salt, sometimes called *Cubic Nitre*, or *Chile Saltpetre*, occurs native, and in enormous quantity, at Tarapaca in Northern Peru, where it forms a regular bed, of great extent, along with gypsum, common salt, and remains of recent shells. The pure salt commonly crystallizes in rhombohedrons, resembling those of calcareous spar. It is deliquescent, and very soluble in water. Sodium nitrate is employed for making nitric acid, but cannot be used for gunpowder, as the mixture burns too slowly, and becomes damp in the air. It has been lately used with some success in agriculture as a superficial manure or top-dressing; also for preparing potassium nitrate (p. 294).

Sodium Phosphates. — The composition and chemical relations of these salts have already been explained in speaking of the basicity of acids (p. 285).

Disodiohydric Phosphate, or *Disodic Orthophosphate; Common Tribasic Phosphate*, $PO_4Na_2H.12OH_2$. — This salt is prepared by precipitating the acid calcium phosphate obtained in decomposing bone-ash by sulphuric acid, with a slight excess of sodium carbonate, and evaporating the clear liquid. It crystallizes in oblique rhombic prisms, which are efflorescent. The crystals dissolve in 4 parts of cold water, and undergo the aqueous fusion when heated. The salt is bitter and purgative; its solution is alkaline to test-paper. Crystals containing 7 molecules of water, and having a form different from that above mentioned, have been obtained.

A *trisodic orthophosphate*, sometimes called *subphosphate*, $PO_4Na_3\ 12OH_2$, is obtained by adding a solution of caustic soda to the preceding salt. The crystals are slender six-sided prisms, soluble in 5 parts of cold water. It is decomposed by acids, even carbonic, but suffers no change by heat, except the loss of its water of crystallization. Its solution is strongly alkaline. A third tribasic phosphate, often called superphosphate or biphosphate, $PO_4NaH_2.OH_2$, may be obtained by adding phosphoric acid to the ordinary phosphate, until it ceases to precipitate barium chloride, and exposing the concentrated solution to cold. The crystals are prismatic, very soluble, and have an acid reaction. When strongly heated, the salt becomes changed into monobasic sodium phosphate, or metaphosphate.

Sodium, Ammonium, and Hydrogen Phosphate; Phosphorous Salt; Microcosmic Salt, $PO_4Na(NH_4)H.4OH_2$. — Six parts of common sodium phosphate are heated with two of water, until the whole is liquefied, and 1 part of powdered sal-ammoniac is added; common salt then separates, and may be removed by a filter, and from the solution, duly concentrated, the microcosmic salt is deposited in prismatic crystals, which may be purified by one or two re-crystallizations. Microcosmic salt is very soluble. When gently heated, it parts with its 4 molecules of crystallization water, and, at a higher temperature, the basic hydrogen is likewise expelled as water, together with ammonia, and a very fusible compound, sodium metaphosphate, remains, which is valuable as a flux in blow-pipe experiments. Microcosmic salt occurs in decomposed urine.

Tetrasodic Phosphate or *Sodium Pyrophosphate*, $P_2O_7Na_4\ 10OH_2$, is prepared by strongly heating common disodic orthophosphate, dissolving the residue in water, and re-crystallizing. The crystals are very brilliant, permanent in the air, and less soluble than the original phosphate: their solution is alkaline. A *sodiohydric pyrophosphate* has been obtained; but it does not crystallize.

Monosodic Phosphate, or *Sodium Metaphosphate*, PO_3Na, is obtained by heating either the acid tribasic phosphate, or microcosmic salt. It is a transparent glassy substance, fusible at a dull red heat, deliquescent, and very soluble in water. It refuses to crystallize, but dries up into a gum-like mass.

If this glassy phosphate be cooled very slowly, it separates as a beautifully crystalline mass. It may be purified by means of boiling water from the vitreous metaphosphate, which will not crystallize. Another metaphosphate has been obtained by adding sodium sulphate to an excess of phosphoric acid, evaporating and heating to upwards of 315° (600° F.). Possibly these several metaphosphates may be represented by the formulæ PO_3Na, $P_2O_6Na_2$, and $P_3O_9Na_3$. (Graham.)

The tribasic phosphates or orthophosphates give a bright-yellow precipitate with solution of silver nitrate; the bibasic and monobasic phosphates afford white precipitates with the same substance. The salts of the two latter classes, fused with excess of sodium carbonate, yield orthophosphoric acid.

Respecting the phosphates intermediate in composition between the metaphosphate and pyrophosphate of sodium, discovered by Fleitmann and Henneberg, see page 287.

Sodium Borates. — The *neutral borate* or *metaborate*, BO_2Na, or $B_2O_3.ONa_2$, is formed by fusing common borax and sodium carbonate in equivalent proportions, and dissolving the mass in water. It forms large crystals containing $BO_2Na.3OH_2$.

The *Anhydroborate*, *Biborate*, or *Borax*, $2BO_2Na.B_2O_3.10OH_2 = 2B_2O_3.ONa_2.10OH_2$, occurs in the waters of certain lakes in Thibet and Persia: it is imported in a crude state from the East Indies under the name of *tincal*. When purified it constitutes the borax of commerce. Much borax is now, however, manufactured from the native boric acid of Tuscany, and also from a native calcium borate called *hayesine*, which occurs in southern Peru. Borax crystallizes in six-sided prisms, which effloresce in dry air, and require 20 parts of cold, and 6 of boiling water for solution. Exposed to heat, the 10 molecules of water of crystallization are expelled, and at a higher temperature the salt fuses, and assumes a glassy appearance on cooling: in this state it is much used for blowpipe experiments, the metallic oxides dissolving in it to transparent beads, many of which are distinguished by characteristic colors. By particular management, crystals of borax can be obtained with 5 molecules of water: they are very hard, and permanent in the air. Although by constitution an acid salt, borax has an alkaline reaction to test-paper, it is used in the arts for soldering metals, its action consisting in rendering the surfaces to be joined metallic, by dissolving the oxides, and it sometimes enters into the composition of the glaze with which stoneware is covered.

Sodium Sulphide, SNa_2. — Prepared in the same manner as potassium monosulphide: it separates from a concentrated solution in octohedral crystals, which are rapidly decomposed by contact with the air into a mixture of sodium hydrate and hyposulphite. It forms double sulphur-salts with hydrogen sulphide, carbon bisulphide, and other sulphur-acids.

Sodium sulphide is supposed to enter into the composition of the beautiful pigment *ultramarine*, which is prepared from the *lapis lazuli*, and is now imitated by artificial means. An intimate mixture of 37 kaolin, 15 sodium sulphate, 22 sodium carbonate, 18 sulphur, and 8 charcoal, is heated from twenty-four to thirty hours in large crucibles. The product thus obtained is again heated in cast-iron boxes at a moderate temperature till the required tint is obtained. After being finely pulverized, washed and dried,

it constitutes commercial ultramarine. The composition of this color varies, and its true constitution is not known.

There is no good precipitant for sodium, all its salts being very soluble, with the exception of the *metantimonate*, which is precipitated on mixing a solution of a sodium salt with a solution of potassium metantimonate; the use of this reagent is, however, attended with some difficulties. The presence of sodium is often determined by negative evidence. The yellow color imparted by sodium salts to the outer flame of the blowpipe, and to combustible matter, is a character of considerable importance. The spectral phenomena exhibited by sodium compounds are mentioned on page 88.

AMMONIUM.

The ammonia salts are most conveniently studied in this place, on account of their close analogy to those of potassium and sodium. These salts are formed by the direct union of ammonia NH_3 with acids, and as already pointed out (p. 163), they may be regarded as compounds of acid radicals, Cl, NO_3, SO_4, &c., with a basylous radical NH_4, called *ammonium*, which plays in these salts the same part as potassium and sodium in their respective compounds; thus:

NH_3 Ammonia.	+	HCl Hydrochloric acid.	=	$NH_4.Cl$ Ammonium chloride.
NH_3	+	HNO_3 Nitric acid.	=	$NH_4.NO_3$ Ammonium nitrate.
NH_3	+	H_2SO_4 Sulphuric acid.	=	$NH_4.H.SO_4$ Acid ammonium sulphate.
$2NH_3$	+	H_2SO_4	=	$(NH_4)_2.SO_4$ Neutral ammonium sulphate.

The radical NH_4 is not capable of existing in the free state, inasmuch as it contains an uneven number of monad atoms: it is simply the residue which is left on removing the atom of chlorine from the saturated molecule N^vH_4Cl. Whether the double molecule N_2H_8, or $\left|\begin{matrix}NH_4\\NH_4\end{matrix}\right.$, has a separate existence, is a different question. Ammonium appears, indeed, to be capable of forming an amalgam with mercury; but even in this state it is quickly resolved into ammonia and free hydrogen.

When a globule of mercury is placed on a piece of moistened potassium hydrate, and connected with the negative side of a voltaic battery of very moderate power, the circuit being completed through the platinum plate upon which the alkali rests, decomposition of the latter takes place, and an amalgam of potassium is rapidly formed. If this experiment be now repeated with a piece of sal-ammoniac instead of potassium hydrate, a soft, solid, metalline mass is also produced, which has been called the *ammoniacal amalgam*, and considered to contain ammonium in combination with mercury. A simpler method of preparing this compound is the following: A little mercury is put into a test-tube with a grain or two of potassium or sodium, and gentle heat applied; combination ensues, attended by

heat and light. When cold, the fluid amalgam is put into a capsule, and covered with a strong solution of sal-ammoniac. The production of an ammoniacal amalgam instantly commences, the mercury increasing prodigiously in volume, and becoming quite pasty. The increase of weight is, however, quite trifling: it varies from $\frac{1}{1800}$ to $\frac{1}{1200}$ part. Left to itself, the amalgam quickly decomposes into fluid mercury, ammonia, and hydrogen; it is quite possible, indeed, that the so-called amalgam may be nothing more than mercury which has absorbed a certain quantity of these gases, just as silver, when heated to a very high temperature, is capable of taking up about twenty times its volume of oxygen gas, which it gives up again on cooling.

The following experiments lately made by Weyl* afford somewhat stronger evidence in favor of the separate existence of ammonium. When lumps of pure bright sodium are placed at one end of a bent tube, a quantity of silver chloride previously saturated with ammonia-gas at the other, the tube then sealed, the end containing the silver-chloride heated in a bath of calcium chloride, and the other end immersed in cold water, the sodium swells up, and is converted into a liquid, which is copper-red by perpendicularly reflected, greenish-yellow by obliquely reflected light, blue in thin films by transmitted light. This liquid is *sodammonium* $N_2H_6Na_2$, that is, ammonium N_2H_8 having two of its hydrogen atoms replaced by sodium. As the silver-chloride cools, and the ammonia-gas is reabsorbed, the sodammonium decomposes and pure sodium remains behind, having a dull surface and spongy texture. By again heating the silver-chloride, the compound may be reproduced any number of times.

Potassammonium, $N_2H_6K_2$?, is prepared like sodammonium, and exhibits similar properties.

Other metallammoniums may be produced by the decomposition of sodium- or potass-ammonium. Thus when a mixture of a metallic chloride or oxide with an equivalent quantity of sodium is exposed in the manner above described to the action of ammonia-gas, the gas is first absorbed by the metallic chloride (or oxide) and afterwards by the sodium, the sodammonium thus formed flowing over the metallic salt, and reacting upon it without much rise of temperature. With a mixture of barium-chloride and sodium the reaction appears to be:

$$\underset{\text{Sodammonium.}}{N_2H_6Na_2} + 2NH_3 + Ba''Cl_2 = \underset{\text{Barammonium.}}{N_2H_6Ba''} + \underset{\substack{\text{Chloride of}\\ \text{Sodammonium.}}}{2NH_3NaCl.}$$

Barammonium forms a deep blue liquid having a metallic lustre. — *Copper-*, *Mercury-*, and *Silver-ammonium* are obtained in like manner from the respective chlorides, and *Zinc-ammonium* from the oxide. These compounds are likewise very unstable, being resolved, even in the sealed tube, into metal (which appears gray, dull, and destitute of coherence) and ammonia. If in the arrangement just described the metallic chloride be replaced by an ammonium-salt, *e.g.*, NH_4Cl or $(NH_4)_2SO_4$, similar reactions take place, and the tube becomes filled with a blue liquid mixed with excess of ammonia. This blue liquid, which is also formed by the action of potassium hydrate on potassammonium, appears to consist of *ammonium* itself, N_2H_8. It is even more unstable than the metallammoniums, being resolved into ammonia and hydrogen, partly even before the reaction between the ammonium-salt and the sodammonium is completed.

But whether ammonium has any separate existence or not, it is quite certain that many ammoniacal salts are isomorphous with those of potassium; and if from any two of the corresponding salts, as the nitrates,

* Pogg. Ann. cxxi. 697.

KNO_3 and NH_4NO_3, we subtract the radical NO_3 common to the two, there remain the metal K and the group NH_4, which are, therefore, supposed to be isomorphous.

Ammonium Chloride, Sal-ammoniac, NH_4Cl. — Sal-ammoniac was formerly obtained from Egypt, being extracted by sublimation from the soot of camels' dung: it is now largely manufactured from the ammoniacal liquid of the gas-works, and from the condensed products of the distillation of bones, and other animal refuse, in the preparation of animal charcoal.

These impure and highly offensive solutions are treated with a slight excess of hydrochloric acid, by which the free alkali is neutralized, and the carbonate and sulphide are decomposed, with evolution of carbonic acid and sulphuretted hydrogen gases. The liquid is evaporated to dryness, and the salt carefully heated, to expel or decompose the tarry matter; it is then purified by sublimation in large iron vessels lined with clay, surmounted with domes of lead.

Sublimed sal-ammoniac has a fibrous texture; it is tough, and difficult to powder.

When crystallized from water it separates, under favorable circumstances, in distinct cubes or octohedrons; but the crystals are usually small, and aggregated together in rays. It has a sharp saline taste, and is soluble in $2\frac{3}{4}$ parts of cold, and in a much smaller quantity of hot water. By heat, it is sublimed without decomposition. The crystals are anhydrous. Ammonium chloride forms double salts with the chlorides of magnesium, nickel, cobalt, iron, manganese, zinc, and copper.

Ammonium Nitrate, $NO_3(NH_4)$, is easily prepared by adding ammonium carbonate to slightly diluted nitric acid until neutralization has been reached. By slow evaporation at a moderate temperature it crystallizes in six-sided prisms, like those of potassium nitrate; but, as usually prepared for making nitrogen monoxide, by quick boiling until a portion solidifies completely on cooling, it forms a fibrous and indistinct crystalline mass.

Ammonium nitrate dissolves in two parts of cold water, producing considerable depression of temperature; it is but feebly deliquescent, and deflagrates like nitre on contact with heated combustible matter. Its decomposition by heat has been already explained (p. 159).

Ammonium Sulphate, $SO_4(NH_4)_2$. — Prepared by neutralizing ammonium carbonate with sulphuric acid, or on a large scale, by adding sulphuric acid in excess to the coal-gas liquor just mentioned, and purifying the product by suitable means. It is soluble in 2 parts of cold water, and crystallizes in long, flattened, six-sided prisms. It is entirely decomposed, and driven off by ignition, and, even to a certain extent, by long boiling with water, ammonia being expelled and the liquid rendered acid.

Ammonium Carbonates. — H. Rose admits the existence of a considerable number of these salts, to which he assigns very complicated formulæ; but, according to H. Sainte Claire-Deville,* there exist only two ammonium carbonates of definite composition, namely:

(*a*) *Ammonium and Hydrogen Carbonate*, or *Mono-ammonic Carbonate*, $CO_3(NH_4)H$, commonly called *Bicarbonate*, or *Acid carbonate of ammonia*. — This salt is obtained by saturating an aqueous solution of ammonia, or of the sesquicarbonate, with carbonic acid gas; or by treating the finely pounded sesquicarbonate with strong alcohol, which dissolves out normal or diammonic carbonate, leaving a residue of the mono-ammonic salt. Cold water may be used instead of alcohol for this purpose; but it dissolves a larger

* Ann. Chim. Phys. [3] xl. 87.

quantity of the mono-ammonic carbonate. All ammonium-carbonates when left to themselves are gradually converted into mono-ammonic carbonate. This salt forms large crystals belonging to the trimetric system. According to Deville it is dimorphous, but never isomorphous with monopotassic carbonate; when exposed to the air, it volatilizes slowly, and gives off a faint ammoniacal odor. It dissolves in 8 parts of cold water, the solution decomposing gradually at ordinary temperatures, quickly when heated above 30° C. (86° F.) with evolution of ammonia. It is insoluble in alcohol, but when exposed to the air, under alcohol, it dissolves as normal carbonate, evolving carbon dioxide.

It has been found native in considerable quantity in the deposits of guano, on the western coast of Patagonia, in white crystalline masses, having a strong ammoniacal odor.

(*b.*) *Tetrammonio-dihydric Carbonate*, $C_3O_9N_4H_{18} = (CO_3)_3(NH_4)_4H_2$. — This salt, commonly called *sesqui-carbonate of ammonia*, contains the elements of 1 molecule of diammonic and 2 molecules of mono-ammonic carbonate, into which it is, in fact, resolved by treatment with water or alcohol:

$$(CO_3)_3(NH_4)_4H_2 \;=\; CO_3(NH_4)_2 \;+\; 2[(CO_3(NH_4)H].$$

It is obtained by dissolving the commercial carbonate in strong aqueous ammonia, at about 30° C. (86° F.) and crystallizing the solution. It forms large transparent rectangular prisms, having their summits truncated by octohedral faces. These crystals decompose very rapidly in the air, giving off water and ammonia, and being converted into mono-ammonic carbonate.

The *normal* or *diammonic carbonate*, $CO_3(NH_4)_2$, has not been obtained in the solid state. Commercial carbonate of ammonia (*sal volatile*, *salt* of *hartshorn*) consists of sesqui-carbonate more or less pure. It is prepared on the large scale by the dry distillation of bones, hartshorn, and other animal matter, and is purified from adhering empyreumatic oil by subliming it once or twice with animal charcoal in cast-iron vessels, over which glass receivers are inverted. Another method consists in heating to redness a mixture of 1 part ammonium chloride or sulphate, and 2 parts calcium carbonate (chalk), or potassium carbonate, in a retort, to which a receiver is luted.*

Ammonium Sulphides. — Several of these compounds exist, and may be formed by distilling with sal-ammoniac the corresponding sulphides of potassium or sodium.

Ammonium and Hydrogen Sulphide, or *Ammonium Sulph-hydrate*, $S(NH_4)H$, is a compound of great practical utility; it is obtained by saturating a solution of ammonia with well-washed sulphuretted hydrogen gas, until no more of the latter is absorbed. The solution is nearly colorless at first, but becomes yellow after a time, without, however, suffering material injury, unless it has been exposed to the air. It gives precipitates with most metallic solutions, which are very often characteristic, and is of great service in analytical chemistry.

Ammoniacal salts are easily recognized; they are all decomposed or volatilized at a high temperature; and when heated with calcium hydrate or solution of alkaline carbonate, they give off ammonia, which may be recog-

[* *Diammonio-hydric Phosphate; Common Tribasic Phosphate*, PO_4, $2(NH_4)H.OH_2$.—This salt is prepared by precipitating the acid calcium phosphate, with an excess of the commercial ammonium carbonate and evaporating at a moderate temperature. It crystallizes in six-sided tables derived from oblique quadrangular prisms The crystals dissolve in 4 parts of water and in alcohol. They are efflorescent, have a saline, alkaline taste and alkaline reaction. The acid tribasic phosphate $PO_4.NH_4.H_2.4OH$ is formed when a solution of the common is boiled as long as ammonia is given off. It crystallizes in 4-sided prisms, which are permanent soluble in five parts of water and have an acid taste and reaction. When ammonia in excess is added to either of these salts, the triammonic phosphate $PO_43(NH_4)$ is deposited as a granular precipitate.—R. B.]

nized by its odor and alkaline reaction. The salts are all more or less soluble; the acid tartrate and the platinochloride being, however, among the least soluble; hence ammonium salts cannot be distinguished from potassium salts by the tests of tartaric acid and platinum solution. When a solution containing an ammoniacal salt, or free ammonia, is mixed with patash, and a solution of *mercuric iodide* in *potassium iodide* is added, a brown precipitate or coloration is immediately produced, consisting of dimercurammonium iodide, $NHg_2''I$:

$$NH_3 + 2Hg''I_2 = NHg''_2I + 3HI.$$

This is called Nessler's test; it is by far the most delicate test for ammonia that is known.

Amic Acids and Amides.

Sulphamic Acid. — When dry ammonia gas is passed over a thin layer of sulphuric oxide SO_3, the gas is absorbed, and a white crystalline powder is formed, having the composition $N_2H_6SO_3$, that is, of ammonium sulphate minus one molecule of water:

$$N_2H_6SO_3 = SO_4(NH_4)_2 - OH_2.$$

It is not, however, a salt of sulphuric acid: for its aqueous solution does not give any precipitate with baryta-water or soluble barium salts. It is, in fact, the ammonium salt of *sulphamic acid*, an acid derived from sulphuric acid, SO_4H_2 or $SO_2(HO)_2$, by substitution of the univalent radical NH_2* for one atom of hydroxyl, HO. The formula of this acid is $SO_3(NH_2)H$, and that of its ammonium salt, $SO_3(NH_2)NH_4$, or $SO_3N_2H_6$. Ammonium sulphamate is permanent in the air, and dissolves without decomposition in water. Its solution, evaporated in a vacuum, over oil of vitriol, yields the salt in transparent colorless crystals.

The solution of the ammonium salt, mixed with baryta-water, gives off ammonia, and yields a solution of *barium sulphamate*, $(SO_3NH_2)_2Ba''$, which may be obtained by evaporation in well defined crystals; and the solution of this salt, decomposed with potassium sulphate, yields *patassium sulphamate*, SO_3NH_2K.

Carbamic Acid. — When dry ammonia gas is mixed with carbon dioxide, the mixture being kept cool, the gases combine in the proportion of 2 volumes of the former to 1 volume of the latter, forming a pungent, very volatile substance, which condenses in white flocks. This substance has the composition $CO_2N_2H_6$, that is, of normal ammonium carbonate, $CO_3(NH_4)_2$, *minus* one molecule of water. It was formerly called *anhydrous carbonate of ammonia;* but, like the preceding salt, is not really a carbonate, but the ammonium salt of *carbamic acid*, $CO_2(NH_2)H$, derived from carbonic acid, CO_3H_2 or $CO(OH)_2$, by substitution of amidogen NH_2 for 1 atom of hydroxyl. Ammonium carbamate dissolves readily in water, and quickly takes up one molecule of that compound, whereby it is converted into ammonium carbonate. When treated with sulphuric oxide, it is converted into ammonium sulphamate.

Carbamide, CON_2H_4. — When ammonia gas is mixed with carbon oxychloride or phosgene gas, $COCl_2$, a white crystalline powder is formed, having this composition:

$$COCl_2 + 2NH_3 = 2HCl + CON_2H_4.$$

This compound, which is likewise formed in other reactions to be afterwards considered, is derived from carbonic acid, $CO(OH)_2$, by substitution

* See page 237.

of 2 atoms of amidogen for 2 atoms of hydroxyl. It differs from carbamic acid in being a neutral substance, not containing any hydrogen easily replaceable by metals.

Other bibasic acids likewise yield an amic acid and a neutral amide by substitution of 1 or 2 atoms of amidogen for hydroxyl. Tribasic acids yield in like manner two amic acids and one neutral amide, and tetrabasic acids may yield three amic acids and a neutral amide; thus, from pyrophosphoric acid, $P_2O_7H_4 = P_2O_3(HO_4)$, are obtained the three amic acids $P_2O_6(NH_2)H_3$, $P_2O_5(NH_2)_2H_2$, and $P_2O_4(NH_2)H$.

Monobasic acids, which contain but one atom of hydroxyl, yield by this mode of substitution only neutral amides, no amic acids: thus, from acetic acid, $C_2H_4O_2 = C_2H_3O_2.HO$, is obtained acetamide, $C_2H_3O(NH_2)$.

The neutral amides may also be regarded as derived from one or more molecules of ammonia, by substitution of univalent or multivalent acid radicals, for hydrogen; thus, acetamide $= N'''H_2(C_2H_3O)$; carbamide $N'''H\,(CO)''$, &c.

By similar substitution of metals, or basylous compound radicals for the hydrogen of ammonia, basic compounds, called *amines*, are formed. Thus, when potassium is gently heated in ammonia gas, *monopotassamine*, NH_2K, is formed. It is an olive-green substance, which is decomposed by water into ammonia and potassium hydrate:

$$NH_2K + OH_2 = NH_3 + OKH.$$

It melts at a little below 100°, and when heated in a close vessel, is resolved into ammonia and *tripotassamine:*

$$3NH_2K = 2NH_3 + NK_3.$$

The latter effervesces violently with water, yielding ammonia and potassium hydrate:

$$NK_3 + 3OH_2 = NH_3 + 3OKH.$$

The formation and properties of amides and amines will be further considered under Organic Chemistry.

Metallammoniums.—We have already spoken of the formation of compounds which may be regarded as derived from ammonium, N_2H_8, by substitution of metals for hydrogen: *e. g.* sodammonium, $N_2H_6Na_2$. Salts of such radicals are also formed in several ways. Ammonia gas is absorbed by various metallic salts in different proportions, forming compounds, some of which may be formulated as salts of metallammoniums. Thus, platinum dichloride, $PtCl_2$, absorbs two molecules of ammonia, forming *platosammonium chloride*, $N_2H_6Pt''.Cl_2$; and platinum tetrachloride, $Pt^{iv}Cl_4$, absorbs four molecules of ammonia, forming *platinammonium chloride*, $N_4H_{12}Pt^{iv}.Cl_4$. In like manner, cupric chloride and sulphate form the *chloride* and *sulphate of cuprammonium*, $N_2H_6Cu''.Cl_2$ and $N_2H_6Cu''.SO_4$.

Similar compounds are formed in many cases by precipitating metallic salts with ammonia or ammoniacal salts: thus, ammonia added to a solution of mercuric chloride, $HgCl_2$, forms a white precipitate, consisting of *dimercurammonium chloride*, $N_2H_4Hg''_2.Cl_2$; and by dropping a solution of mercuric chloride into a boiling solution of sal-ammoniac mixed with free ammonia, crystals are obtained, consisting of *mercurammonium chloride*, $N_2H_4Hg''.Cl_2$. Some of these compounds will be further considered in connection with the several metals.

LITHIUM.

Atomic weight, 7. Symbol, Li.

Lithium is found in petalite, spodumene, lepidolite, triphylline, and a few other minerals, and sometimes occurs in minute quantities in mineral springs.

The metal is obtained by fusing pure lithium chloride in a small thick porcelain crucible, and decomposing the fused chloride by electricity. It is a white metal like sodium, and very oxidizable. Lithium fuses at 180° C. (356° F.); its specific gravity is 0·59: it is, therefore, the lightest solid known.

A lithium salt may be obtained from petalite on the small scale, by the following process: The mineral is reduced to an exceedingly fine powder, mixed with five or six times its weight of pure calcium carbonate, and the mixture heated to whiteness, in a platinum crucible placed within a well covered earthen one, for twenty minutes or half an hour. The shrunken coherent mass is digested in dilute hydrochloric acid, the whole evaporated to dryness, acidulated water added, and the silica separated by a filter. The solution is then mixed with ammonium carbonate in excess, boiled, and filtered; the clear liquid is evaporated to dryness, and gently heated in a platinum crucible, to expel the sal-ammoniac; and the residue is wetted with oil of vitriol, gently evaporated once more to dryness, and ignited: pure fused lithium sulphate then remains.

This process will serve to give a good idea of the general nature of the operation by which alkalies are extracted in mineral analysis, and their quantities determined.

Lithium hydrate, LiHO, is much less soluble in water than the hydrates of potassium and sodium; the *carbonate* and *phosphate* are also sparingly soluble salts. The *chloride* crystallizes in anhydrous cubes which are deliquescent. *Lithium sulphate* is a very beautiful salt; it crystallizes in lengthened prisms containing one molecule of water. It gives no double salt with aluminium sulphate.

The salts of lithium color the outer flame of the blowpipe carmine-red. The spectral phenomena exhibited by lithium compounds are mentioned on page 89.

CÆSIUM AND RUBIDIUM.

Cs = 133. — Rb = 85·4.

The two metals designated by these names were discovered by Bunsen and Kirchhoff by means of their spectrum apparatus mentioned on page 88: the former in 1860 and the latter in 1861. These metals, it appears, are widely diffused in nature, but always occur in very small quantities; they have been detected in many mineral waters, as well as in some minerals, namely, lithia-mica or lepidolite, and petalite; lately also in felspar; they have also been found in the alkaline ashes of the beet-root. The brine of Dürkheim has up to the present moment been the richest source of cæsium. The best material for the preparation of rubidium, is lepidolite, which has been found to contain as much as 0·2 per cent. of that metal. Both metals are closely analogous to potassium in their deportment, and cannot be distinguished from that metal or from one another, either by reagents or before the blowpipe.

Rubidium and cæsium, like potassium, form double salts with tetrachloride of platinum, which are, however, much more insoluble than the corresponding potassium salts: it is on this property that the separation of these metals from potassium is based. The mixture of platinochlorides is repeatedly extracted with boiling water, when a difficultly soluble residue, consisting chiefly of the platinochlorides of cæsium and rubidium, remains.

The hydrates of these new metals are powerful bases, which attract carbonic acid from the air, passing, first into normal carbonate and then into acid carbonate. Cæsium carbonate is soluble in absolute alcohol; rubidium carbonate is nearly insoluble in that liquid: this property is made use of for the separation of these two metals. The chloride crystallizes in cubes, and is somewhat more soluble in water than chloride of potassium.

Rubidium chloride, when in a state of fusion, is easily decomposed by the electric current; the metal produced rises to the surface and burns with a reddish light. If this experiment be performed in an atmosphere of hydrogen, to prevent oxidation, the separated metal is nevertheless lost, dissolving as it does in the fused chloride, which is transformed into a subchloride having the blue color of smalt. Rubidium, when separated under mercury by the electric current, forms a crystalline amalgam of silvery lustre, which is rapidly oxidized by the air, and decomposes water in the cold. Cæsium chloride, under the influence of the electric current, exhibits exactly the same deportment as rubidium choride. Rubidium is electro-positive towards potassium, cæsium is electro-positive towards rubidium and potassium, and thus constitutes the most electro-positive member of the elements.

SILVER.

Atomic weight, 108. Symbol, Ag (Argentum).

Silver is found in the metallic state, as sulphide, in union with sulphide of antimony and sulphide of arsenic, also as chloride, iodide, and bromide. Among the principal silver mines may be mentioned those of the Hartz mountains in Germany, of Kongsberg in Norway, and, more particularly, of the Andes, in both North and South America.

The greater part of the silver of commerce is extracted from ores so poor as to render any process of *smelting* or fusion inapplicable, even where fuel could be obtained, and this is often difficult to be procured. Recourse, therefore, is had to another method — that of *amalgamation* — founded on the easy solubility of silver and many other metals in metallic mercury.

The amalgamation process adopted in Germany—which differs somewhat from that in use in America — is as follows: The ore is crushed to powder, mixed with a quantity of common salt, and roasted at a low red heat in a suitable furnace, by which treatment any sulphide of silver it may contain is converted into chloride. The mixture of earthy matter, oxides of iron, copper, soluble salts, silver chloride, and metallic silver, is sifted and put into large barrels made to revolve on axes, with a quantity of water and scraps of iron, and the whole is agitated together for some time, during which the iron reduces the silver chloride to the state of metal. A certain proportion of mercury is then introduced, and the agitation repeated: the mercury dissolves out the silver, together with gold, if there be any, metallic copper, and other substances, forming a fluid amalgam easily separable from the thin mud of earthy matter by subsidence and washing. This amalgam is strained through a strong linen cloth, and the solid portion

exposed to heat in a kind of retort, by which the remaining mercury is distilled off and the silver left behind in an impure state.

Considerable loss often occurs in the amalgamation process from the combination of a portion of the mercury with sulphur, oxygen, &c., whereby it is brought into a pulverulent condition, known as "flouring," and is then liable to be washed away, together with the silver it has taken up. This inconvenience may be prevented, as suggested by Mr. Crookes, by amalgamating the mercury with 1 or 2 per cent. of sodium, which by its superior affinity for sulphur and oxygen, prevents the mercury from becoming floured.

A considerable quantity of silver is obtained from argentiferous galena: in fact, almost every specimen of native lead sulphide is found to contain traces of this metal. When the proportion rises to a certain amount, it becomes worth extracting. The ore is reduced in the usual manner, the whole of the silver remaining with the lead; the latter is then re-melted in a large vessel, and allowed to cool slowly until solidification commences. The portion which first crystallizes is nearly pure lead, the alloy with silver being *more fusible than lead itself:* by particular management this is drained away, and is found to contain nearly the whole of the silver [Pattinson's process]. This rich mass is next exposed to a red heat on the shallow hearth of a furnace, while a stream of air is allowed to impinge upon its surface; oxidation takes place with great rapidity, the fused oxide or litharge being constantly swept from the metal by the blast. When the greater part of the lead has been thus removed, the residue is transferred to a *cupel* or shallow dish made of bone-ashes, and again heated: the last portion of the lead is now oxidized, and the oxide sinks in a melted state into the porous vessel, while the silver, almost chemically pure, and exhibiting a brilliant surface, remains behind.

Pure silver may be easily obtained. The metal is dissolved in nitric acid: if it contains copper, the solution will have a blue tint; gold will remain undissolved as a black powder. The solution is mixed with hydrochloric acid or with common salt, and the white, insoluble, curdy precipitate of silver chloride is washed and dried. This is then mixed with about twice its weight of anhydrous sodium carbonate, and the mixture, placed in an earthen crucible, is gradually raised to a temperature approaching whiteness, during which the sodium carbonate and the silver chloride react upon each other; carbon dioxide and oxygen escape, while metallic silver and soda chloride result: the former melts into a button at the bottom of the crucible, and is easily detached. The following is perhaps the most simple method for the reduction of silver chloride. The silver-salt is covered with water, to which a few drops of sulphuric acid are added; a plate of zinc is then introduced. The silver chloride soon begins to decompose, and is, after a short time, entirely converted into metallic silver; the silver thus obtained is gray and spongy; it is ultimately purified by washing with slightly acidulated water.

Pure silver has a most perfect white color and a high degree of lustre: it is exceedingly malleable and ductile, and is probably the best conductor both of heat and electricity known. Its specific gravity is 10·5. In hardness it lies between gold and copper. It melts at a bright red heat, about 1023° C, (1873° F.), according to the observation of Mr. Daniell. Silver is unalterable by air and moisture: it refuses to oxidize at any temperature, but possesses the extraordinary faculty already noticed of absorbing many times its volume of oxygen when strongly heated in an atmosphere of that gas, or in common air. The oxygen is again disengaged at the moment of solidification, and gives rise to the peculiar arborescent appearance often remarked on the surface of masses or buttons of pure silver. The addition of 2 per cent. of copper is sufficient to prevent the absorption of oxygen.

Silver oxidizes when heated with fusible siliceous matter, as glass, which it stains yellow or orange, from the formation of a silicate. It is little attacked by hydrochloric acid; boiling oil of vitriol converts it into sulphate, with evolution of sulphurous oxide; nitric acid, even dilute and in the cold, dissolves it readily. The tarnishing of surfaces of silver exposed to the air is due to hydrogen sulphide, the metal having a strong attraction for sulphur.

Silver Chlorides. — Two of these compounds are known containing respectively 1 and 2 atoms of silver to 1 atom of chlorine; the second, however, is a very unstable compound.*

The *Monochloride* or *Argentic Chloride*, Ag Cl, is almost invariably produced when a soluble silver salt and a soluble chloride are mixed. It falls as a white curdy precipitate, quite insoluble in water and nitric acid; but one part of silver chloride is soluble in 200 parts of hydrochloric acid when concentrated, and in about 600 parts when diluted with double its weight of water. When heated it melts, and on cooling becomes a grayish crystalline mass, which cuts like horn: it is found native in this condition, constituting the *horn-silver* of the mineralogist. Silver chloride is decomposed by light, both in the dry and in the wet state, very slowly if pure, and quickly if organic matter be present: it is reduced also when put into water with metallic zinc or iron. It dissolves with great ease in ammonia and in a solution of potassium cyanide. In practical analysis the proportion of chlorine or hydrochloric acid in a compound is always estimated by precipitation with silver solution. The liquid is acidulated with nitric acid, and an excess of silver nitrate added; the chloride is collected on a filter, or better by subsidence, washed, dried, and fused; 100 parts correspond to 24·7 of chlorine, or 25·43 of hydrochloric acid.

Argentous Chloride, Ag_4Cl_2, is obtained by treating the corresponding oxide with hydrochloric acid or by precipitating an argentous salt, the citrate, for example, with common salt. It is easily resolved by heat or by ammonia into argentic chloride and metallic silver.

Silver Fluoride, AgF, is produced by dissolving argentic oxide or carbonate in aqueous hydrofluoric acid, and separates on evaporation in transparent quadratic octohedrons, which contain $AgF.OH_2$, and give off their water when fused. Their solution gives, with hydrochloric acid, a precipitate of argentic chloride. When chlorine gas is passed over fused silver fluoride, silver chloride is formed and fluorine is set free (p. 192).

Silver Iodide, AgI, is a pale-yellow insoluble precipitate, produced by adding silver nitrate to potassium iodide; it is insoluble, or nearly so, in ammonia, and in this respect forms an exception to the silver-salts in general. Deville has obtained a crystalline silver iodide by the action of concentrated hydriodic acid upon metallic silver, which it dissolves with disengagement of hydrogen. Hydriodic acid converts silver chloride into iodide. The *bromide* of silver very closely resembles the chloride.

Silver Oxides. — There are three oxides of silver, only one of which can, however, be regarded as a well-defined compound, namely:

The *Monoxide* or *Argentic Oxide*, OAg_2. — This oxide is a powerful base,

* The existence of two silver chlorides is utterly incompatible with the hypothesis that both silver and chlorine are monad elements. The composition of the argentous compounds is not perhaps very well established; but supposing the chloride to contain Cl_2Ag_4, as usually stated, its constitution may be represented by the formula $\left|\begin{matrix}ClAg_2\\ClAg_2\end{matrix}\right.$, in which the chlorine plays the part of a triad.

yielding salts isomorphous with those of the alkali-metals. It is obtained as a pale-brown precipitate on adding caustic potash to a solution of silver nitrate:

$2NO_3Ag$	+	OKH	=	OAg_2	+	NO_3K	+	NO_3H
Silver nitrate.		Potassium hydrate.		Silver oxide.		Potassium nitrate.		Hydrogen nitrate.

It is very soluble in ammonia, and is dissolved also to a small extent by pure water; the solution is alkaline. Recently precipitated silver chloride, boiled with a solution of caustic potash of specific gravity 1·25, is converted, according to Gregory, although with difficulty, into argentic oxide, which in this case is black and very dense. Argentic oxide neutralizes acids completely, and forms, for the most part, colorless salts. It is decomposed by a red-heat, with evolution of oxygen, spongy metallic silver being left; the sun's rays also effect its decomposition to a small extent.

Argentous Oxide, OAg_4.*— When dry argentic citrate is heated to 100° in a stream of hydrogen gas, it loses oxygen and becomes dark-brown. The product, dissolved in water, gives a dark-colored solution containing free citric acid and argentous citrate, which when mixed with potash yields a precipitate of argentous oxide. This oxide is a black powder, very easily decomposed, and soluble in ammonia. The solution of argentous citrate is rendered colorless by heat, being resolved into argentic citrate and metallic silver. According to Wöhler, argentous oxide is also formed by boiling argentic arsenite with caustic alkalies. In this case it is mixed with metallic silver.

Silver Dioxide, O_2Ag_2 or $\left|\begin{matrix}OAg\\OAg\end{matrix}\right.$. — This is a black crystalline substance which forms upon the positive electrode of a voltaic arrangement employed to decompose a solution of silver nitrate. It is reduced by heat, evolves chlorine when acted upon by hydrochloric acid, explodes when mixed with phosphorus and struck, and decomposes solution of ammonia, with great energy and rapid disengagement of nitrogen gas.

Silver Nitrate or Argentic Nitrate, NO_3Ag. — This salt is prepared by dissolving silver in nitric acid, and evaporating the solution to dryness, or until it is strong enough to crystallize on cooling. The crystals are colorless, transparent, anhydrous tables, soluble in an equal weight of cold, and in half that quantity of boiling water; they also dissolve in alcohol. They fuse when heated, like those of nitre, and at a high temperature suffer decomposition: the *lunar caustic* of the surgeon is silver nitrate which has been melted and poured into a cylindrical mould. The salt blackens when exposed to light, more particularly if organic matters of any kind are present, and is frequently employed to communicate a dark stain to the hair; it enters into the composition of the "indelible" ink used for marking linen. The black stain has been thought to be metallic silver; it may possibly be argentous oxide. Pure silver nitrate may be prepared from the metal alloyed with copper: the alloy is dissolved in nitric acid, the solution evaporated to dryness, and the mixed nitrates cautiously heated to fusion. A small portion of the melted mass is removed from time to time for examination; it is dissolved in water, filtered, and ammonia added to it in excess. While any copper-salt remains undecomposed, the liquid will be blue, but when that no longer happens, the nitrate may be suffered to cool, dissolved in water, and filtered from the insoluble black oxide of copper.

* If this formula be correct, oxygen must be a tretrad.

Silver Sulphate, SO_4Ag_2. — The sulphate may be prepared by boiling together oil of vitriol and metallic silver, or by precipitating a concentrated solution of silver nitrate with an alkaline sulphate. It dissolves in 88 parts of boiling water, and separates in great measure in the crystalline form on cooling, having but a feeble degree of solubility at a low temperature. It forms with ammonia a crystallizable compound which is freely soluble in water, contains $SO_4Ag_2 . 2NH_3$, and may therefore be regarded as *argentammonium sulphate*, $SO_4(NH_3Ag)_2$.

Silver hyposulphate, $S_2O_6Ag_2.OH_2$, is a soluble crystallizable salt, permanent in the air. The *hyposulphite* is insoluble, white, and very prone to decomposition: it combines with the alkaline hyposulphites, forming soluble compounds distinguished by an intensely sweet taste. The alkaline hyposulphites dissolve both oxide and chloride of silver, and give rise to similar salts, an oxide or chloride of the alkaline metal being at the same time formed: hence the use of alkaline hyposulphites in fixing photographic pictures (p. 97). *Silver carbonate* is a white insoluble substance obtained by mixing solutions of silver nitrate and sodium carbonate. It is blackened and decomposed by boiling.

Silver Sulphide, SAg_2. — This is a soft, gray, and somewhat malleable substance, found native in the crystallized state, and easily produced by melting together its constituents, or by precipitating a solution of silver with hydrogen sulphide. It is a strong sulphur-base, and combines with the sulphides of antimony and arsenic: examples of such compounds are found in the beautiful minerals, *dark* and *light-red silver ore*.

Ammonia-compound of Silver; Berthollet's Fulminating Silver. — When precipitated, argentic oxide is digested in ammonia, a black substance is produced, possessing extremely dangerous explosive properties. While moist, it explodes when rubbed with a hard body, but when dry the touch of a feather is sufficient. The ammonia retains some of this substance in solution, and deposits it in small crystals by spontaneous evaporation. A similar compound exists containing oxide of gold. It is easy to understand the reason why these bodies are subject to such violent and sudden decomposition by the slightest cause, on the supposition that they contain an oxide of an easily reducible metal and ammonia: the attraction between the two constituents of the substance is very feeble, while that between the oxygen of the one and the hydrogen of the other is very powerful. The explosion is caused by the sudden evolution of nitrogen gas and aqueous vapor, the metal being set free.

Soluble silver salts are perfectly characterized by the white curdy precipitate of silver chloride, darkening by exposure to light, and insoluble in hot nitric acid, which is produced by the addition of any soluble *chloride*. Lead and mercury are the only metals which can be confounded with silver in this respect; but lead chloride is soluble to a great extent in boiling water, and is deposited in brilliant acicular crystals when the solution cools; and mercurous chloride is instantly blackened by ammonia, whereas silver chloride is dissolved thereby.

Solutions of silver are reduced to the metallic state by *iron*, *copper*, *mercury*, and other metals. They give with *hydrogen sulphide* a black precipitate of argentic sulphide insoluble in ammonium sulphide; with *caustic alkalies*, a brown precipitate of argentic oxide; and with *alkaline carbonates*, a white precipitate of argentic carbonate, both precipitates being easily soluble in ammonia. Ordinary *sodium phosphate* forms a yellow precipitate

of argentic orthophosphate; *potassium chromate* or *bichromate*, a red-brown precipitate of argentic chromate.

The economical uses of silver are many: it is admirably adapted for culinary and other similar purposes, not being attacked in the slightest degree by any of the substances used for food. It is necessary, however, in these cases, to diminish the softness of the metal by a small addition of copper. The standard silver of England contains 222 parts of silver and 18 parts of copper.

CLASS II.—DYAD METALS.

GROUP I.—METALS OF THE ALKALINE EARTHS.

BARIUM.*

Atomic weight, 137. Symbol, Ba.

THIS metal occurs abundantly as sulphate and carbonate, forming the *veinstone* in many lead mines. Davy obtained it in the metallic state by means similar to those described in the case of lithium. Bunsen subjects barium chloride mixed up to a paste with water and a little hydrochloric acid, at a temperature of 100°, to the action of the electric current, using an amalgamated platinum wire as the negative pole. In this manner the metal is obtained as a solid, highly crystalline amalgam, which, when heated in a stream of hydrogen, yields barium in the form of a tumefied mass, tarnished on the surface, but often exhibiting a silver-white lustre in the cavities. Barium may also be obtained, though impure, by passing vapor of potassium over the red-hot chloride or oxide of barium. It is malleable, melts below a red heat, decomposes water, and gradually oxidizes in the air.

BARIUM CHLORIDE, $BaCl_2 . OH_2$. — This valuable salt is prepared by dissolving the native carbonate in hydrochloric acid, filtering the solution, and evaporating until a pellicle begins to form at the surface: the solution on cooling deposits crystals. When native carbonate cannot be procured, the native sulphate may be employed in the following manner: — The sulphate is reduced to fine powder, and intimately mixed with one third of its weight of powdered coal; the mixture is pressed into an earthen crucible to which a cover is fitted, and exposed for an hour or more to a high red heat, by which the sulphate is converted into sulphide at the expense of the combustible matter of the coal; the black mass thus obtained is powdered and boiled in water, by which the sulphide is dissolved; and the solution, filtered hot, is mixed with a slight excess of hydrochloric acid. Barium chloride and hydrogen sulphide are then produced, the latter escaping with effervescence. Lastly, the solution is filtered to separate any little insoluble matter, and evaporated to the crystallizing point.

The crystals of barium chloride are flat four-sided tables, colorless and transparent. They contain two molecules of water, easily driven off by heat. 100 parts of water dissolve 43·5 parts at 15·5°, and 78 parts at 104·5°, which is the boiling-point of the saturated solution.

BARIUM MONOXIDE, BARYTA, BaO. — The best method of preparing this compound is to decompose the crystallized nitrate by heat in a capacious porcelain crucible until red vapors are no longer disengaged: the nitric

* From *βαρύς*, heavy, in allusion to the great specific gravity of the native carbonate and sulphate.

acid is resolved into nitrous acid and oxygen, and the baryta remains behind in the form of a grayish spongy mass, fusible at a high degree of heat. When moistened with water, it combines into a hydrate, with great elevation of temperature.

Barium Hydrate, $BaH_2O_2 = BaO . H_2O$. — This compound is prepared on a large scale by decomposing a hot concentrated solution of barium chloride with a solution of caustic soda; on cooling, crystals of barium hydrate are deposited, which may be purified by re-crystallization. In the laboratory the barium hydrate is often prepared by decomposing the sulphide with black oxide of copper. (See barium sulphide.) The crystals of barium hydrate contain $BaH_2O_2 . 8$ aq.;* they fuse easily, and lose their water of crystallization when strongly heated.

The hydrate is a white, soft powder, having a great attraction for carbonic acid, and soluble in 20 parts of cold and 2 parts of boiling water. Solution of barium hydrate is a valuable reagent: it is highly alkaline to test-paper, and instantly rendered turbid by the smallest trace of carbonic acid.

Barium Dioxide, BaO_2. — This oxide may be formed, as already mentioned, by exposing baryta, heated to full redness in a porcelain tube, to a current of pure oxygen gas. The dioxide is gray, and forms with water a white hydrate, which is not decomposed by that liquid in the cold, but dissolves in small quantity. Barium hydrate, when heated to redness in a current of dry atmospheric air, loses its water, and is converted, by absorption of oxygen, into barium dioxide, from which the second atom of oxygen may be expelled at a higher temperature. Boussingault has proposed to utilize these reactions for the preparation of oxygen upon a large scale. The dioxide may also be made by heating pure baryta to redness in a platinum crucible, and then gradually adding an equal weight of potassium chlorate, whereby barium dioxide and potassium chloride are produced. The latter may be extracted by cold water, and the dioxide left in the state of hydrate. It is interesting chiefly in its relation to hydrogen dioxide. When dissolved in dilute acid, it is decomposed by potassium bichromate, and by the oxide, chloride, sulphate, and carbonate of silver.

Barium Nitrate, $(NO_3)_2Ba$. — The nitrate is prepared by methods exactly similar to those adopted for preparing the chloride, nitric acid being substituted for hydrochloric. It crystallizes in transparent colorless octohedrons, which are anhydrous. They require for solution 8 parts of cold, and 3 parts of boiling water. This salt is much less soluble in dilute nitric acid than in pure water: errors sometimes arise from such a precipitate of crystalline barium nitrate being mistaken for sulphate. It disappears on heating, or by large affusion of water.

Barium Sulphate, SO_4Ba. — Found native as *heavy* spar or *barytes*, often beautifully crystallized: its specific gravity is as high as 4·4 to 4·8. This compound is always produced when sulphuric acid or a soluble sulphate is mixed with a solution of a barium salt. It is not sensibly soluble in water or in dilute acids: even in nitric it is almost insoluble: hot oil of vitriol dissolves a little, but the greater part separates again on cooling. Barium sulphate is now produced artificially on a large scale; it is used as a substitute for white lead in the manufacture of oil-paints. The sulphate to be used for this purpose is precipitated from very dilute solutions: it is known in commerce as *blanc fixe*. Powdered native barium sulphate, being

* The symbol aq. (abbreviation of *aqua*) is often used to denote water of crystallization.

rather crystalline, has not sufficient body. For the production of sulphate, the chloride of barium is first prepared, which is dissolved in a large quantity of water, and then precipitated by dilute sulphuric acid.

Barium Carbonate, CO_3Ba. — The natural carbonate is called *witherite*: the artificial is formed by precipitating the chloride or nitrate with an alkaline carbonate, or carbonate of ammonia. It is a heavy, white powder, very sparingly soluble in water, and chiefly useful in the preparation of the rarer barium salts.

Barium Sulphides. — The *monosulphide*, BaS, is obtained in the manner already described; the higher sulphides may be formed by boiling it with sulphur. Barium monosulphide crystallizes from a hot solution in thin, nearly colorless plates, which contain water, and are not very soluble: they are rapidly altered by the air. A strong solution of this sulphide may be employed in the preparation of barium hydrate, by boiling it with small successive portions of black oxide of copper, until a drop of the liquid ceases to form a black precipitate with lead salts; the filtered liquid on cooling yields crystals of the hydrate. In this reaction, besides hydrate of barium, the hyposulphate of that base, and sulphide of copper, are produced; the latter is insoluble, and is removed by the filter, while most of the hyposulphate remains in the mother-liquor.

Solutions of barium hydrate, nitrate, and chloride, are constantly kept in the laboratory as chemical tests, the first being employed to effect the separation of carbonic acid from certain gaseous mixtures, and the two latter to precipitate sulphuric acid from solution.

Soluble barium salts are poisonous, which is not the case with those of the base next to be described. For their reactions, see p. 332.

STRONTIUM.

Atomic weight, 87·5. Symbol, Sr.

The metal strontium may be obtained from its oxide by means similar to those described in the case of barium: it is usually described as a white metal, heavy, oxidizable in the air, and capable of decomposing water at common temperatures. Matthiessen states, however, that it has a dark-yellow color, and specific gravity 2·54. He prepares it by filling a small crucible having a porous cell with anhydrous strontium chloride mixed with some ammonium chloride, so that the level of the fused chloride in the cell is much higher than in the crucible. The negative pole placed in the cell consists of a very fine iron wire. The positive pole is an iron cylinder placed in the crucible round the cell. The heat is regulated so that a crust forms in the cell, and the metal collects under this crust.

Strontium Monoxide; Strontia; SrO. — This compound is best prepared by decomposing the nitrate with aid of heat: it resembles in almost every particular the earth baryta, forming, like that substance, a white hydrate, soluble in water. A hot saturated solution deposits crystals on cooling, which contain SrH_2O_2. 8 aq.: heated to dull redness they lose the whole of their water, anhydrous strontia being left. The hydrate has a great attraction for carbonic acid.

Strontium Dioxide, SrO_2 — Prepared in the same manner as barium dioxide: it may be substituted for the latter in making hydrogen dioxide.

The native carbonate and sulphate of strontium serve for the preparation of the various salts by means exactly similar to those already described in the case of barium salts: they have a very feeble degree of solubility in water.

Strontium Chloride, $SrCl_2$. — The chloride crystallizes in colorless needles or prisms, which are slightly deliquescent, and soluble in 2 parts of cold and a still smaller quantity of boiling water: they are also soluble in alcohol, and the solution, when kindled, burns with a crimson flame. The crystals contain 6 molecules of water, which they lose by heat: at a higher temperature the chloride fuses.

Strontium Nitrate, $(NO_3)_2Sr$. — This salt crystallizes in anhydrous octohedrons, which require for solution 5 parts of cold, and about half their weight of boiling water. It is principally of value to the pyrotechnist, who employs it in the composition of the well-known "red-fire."*

The spectral phenomena exhibited by strontium compounds are mentioned on page 89.

CALCIUM.

Atomic weight, 40. Symbol, Ca.

Calcium is one of the most abundant and widely diffused of the metals, though it is never found in the free state. As carbonate, it occurs in a great variety of forms, constituting, as limestone, entire mountain-ranges. Calcium was obtained in an impure state by Davy, by means similar to those adopted for the preparation of barium. Matthiessen prepares the pure metal by fusing a mixture of two molecules of calcium chloride and one of strontium chloride with some chloride of ammonium in a small porcelain crucible, in which an iron cylinder is placed as positive pole, and a pointed iron wire or a little rod of carbon connected with the zinc of the battery is made to touch the surface of the liquid. The reduced metal fuses and drops off from the point of the iron wire, and the bead is removed from the liquid by a small iron spatula. Liès-Bodart and Gobin† prepare calcium by igniting the iodide with an equivalent quantity of sodium in an iron crucible having its lid screwed down.

Calcium is a light yellow metal of sp. gr. 1·5778. It is about as hard as gold, very ductile, and may be cut, filed, or hammered out into plates as thin as the finest paper. It tarnishes slowly in dry, more quickly in damp air, decomposes water quickly, and is still more rapidly acted upon by dilute acids. Heated on platinum foil over a spirit-lamp, it burns with a bright flash; with a brilliant light also when heated in oxygen or chlorine gas, or in vapor of bromine, iodine, or sulphur.

Calcium Chloride, $CaCl_2$, is usually prepared by dissolving marble in hydrochloric acid; also a by-product in several chemical manufactures.

* Red Fire:	Grains.	Green Fire:	Grains.
Dry strontium nitrate	800	Dry barium nitrate	450
Sulphur	225	Sulphur	150
Potassium chlorate	200	Potassium chlorate	100
Lampblack	50	Lampblack	25

The strontium or barium-salt, the sulphur and the lampblack, must be finely powdered and intimately mixed, after which the potassium chlorate should be added in rather coarse powder, and mixed, without much rubbing, with the other ingredients. The red fire composition has been known to ignite spontaneously.

† Comptes Rendus, xlvii. 23.

The salt separates from a strong solution in colorless, prismatic, and exceedingly deliquescent crystals, which contain 6 molecules of water. By heat this water is expelled, and by a temperature of strong ignition the salt is fused. The crystals reduced to powder are employed in the production of artificial cold by being mixed with snow or powdered ice; and the chloride, strongly dried or in the fused state, is of great practical use in desiccating gases, for which purpose the latter are slowly transmitted through tubes filled with fragments of the salt. Calcium chloride is also freely soluble in alcohol, which, when anhydrous, forms with it a definite crystallizable compound.

Calcium Fluoride; Fluor-spar; CaF_2. — This substance is important as the most abundant natural source of hydrofluoric acid and the other fluorides. It occurs beautifully crystallized, of various colors, in lead-veins, the crystals having commonly the cubic, but sometimes the octohedral form, parallel to the faces of which latter figure they always cleave. Some varieties, when heated, emit a greenish, and some a purple phosphorescent light. The fluoride is quite insoluble in water, and is decomposed by oil of vitriol in the manner already mentioned (p. 192).

Calcium Monoxide; Lime; CaO. — This extremely important compound may be obtained in a state of considerable purity by heating to full redness for some time fragments of the black bituminous marble of Derbyshire or Kilkenny. If required absolutely pure, it must be made by igniting to whiteness, in a platinum crucible, an artificial calcium carbonate, prepared by precipitating the nitrate with ammonia carbonate. Lime in an impure state is prepared for building and agricultural purposes by calcining, in a kiln of suitable construction, the ordinary limestones which abound in many districts; a red heat, continued for some hours, is sufficient to disengage the whole of the carbonic acid. In the best contrived lime-kilns the process is carried on continuously, broken limestone and fuel being constantly thrown in at the top, and the burned lime raked out at intervals from beneath. Sometimes, when the limestone contains silica, and the heat has been very high, the lime refuses to slake, and is said to be *over-burned;* in this case a portion of silicate has been formed.

Pure lime is white, and often of considerable hardness; it is quite infusible, and phosphoresces, or emits a pale light at a high temperature. When moistened with water, it slakes with great violence, evolving heat, and crumbling to a soft, white, bulky powder, which is a hydrate containing a single molecule of water: the latter can be again expelled by red-heat. This hydrate, CaH_2O_2 or $CaO.OH_2$, is soluble in water, but far less so than either the hydrate of barium or of strontium, and, what is very remarkable, the *colder* the water, the larger is the quantity of the compound that is taken up. A pint of water at 15·5° C. (60° F.) dissolves about 11 grains, while at 100° C. ((212° F.) only 7 grains are retained in solution. The hydrate has been obtained in thin delicate crystals by slow evaporation under the air-pump. Lime-water is always prepared for chemical and pharmaceutical purposes by agitating cold water with excess of calcium hydrate in a closely stopped vessel, and then, after subsidence, pouring off the clear liquid, and adding a fresh quantity of water, for another operation: there is not the least occasion for filtering the solution. Lime-water has a strong alkaline reaction, a nauseous taste, and when exposed to the air becomes almost instantly covered with a pellicle of carbonate, by absorption of carbonic acid. It is used, like baryta-water, as a test for carbonic acid, and also in medicine. Lime-water prepared from some varieties of limestone may contain potash.

The hardening of mortars and cements is in a great measure due to the

gradual absorption of carbonic acid; but even after a very great length of time, this conversion into carbonate is not complete. Mortar is known, under favorable circumstances, to acquire extreme hardness with age. Lime-cements which resist the action of water contain iron oxides, silica, and alumina: they require to be carefully prepared, and the stone not overheated. When they are ground to powder and mixed with water, solidification speedily ensues, from causes not yet thoroughly understood, and the cement, once in this condition, is unaffected by wet. Parker's or Roman cement is made in this manner from the nodular masses of calcareo-argillaceous ironstone found in the London clay. Lime is of great importance in agriculture: it is found more or less in every fertile soil, and is often very advantageously added by the cultivator. The decay of vegetable fibre in the soil is thereby promoted, and other important objects, as the destruction of certain hurtful compounds of iron in marsh and peat-land, are often attained. The addition of lime probably serves likewise to liberate potassium from the insoluble silicate of that base contained in the soil.

Calcium Dioxide, CaO_2. — This compound is stated to resemble barium dioxide, and to be obtainable by treating lime with hydrogen dioxide.

Calcium Sulphate; SO_4Ca. — Crystalline native calcium sulphate, containing two molecules of water, is found in considerable abundance in some localities as *gypsum:* it is often associated with rock-salt. When regularly crystallized, it is termed *selenite.* Anhydrous calcium sulphate is also occasionally met with. The salt is formed by precipitation, when a moderately concentrated solution of calcium chloride is mixed with sulphuric acid. Calcium sulphate is soluble in about 500 parts of cold water, and its solubility is a little increased by heat. It is more soluble in water containing ammonium chloride or potassium nitrate. The solution is precipitated by alcohol. Gypsum, or native hydrated calcium sulphate, is largely employed for the purpose of making casts of statues and medals, and also for moulds in the porcelain and earthenware manufactures, and for other applications. It is exposed to heat in an oven where the temperature does not exceed 127° C. (260° F.), by which the water of crystallization is expelled, and it is afterwards reduced to a fine powder. When mixed with water, it solidifies after a short time, from the re-formation of the same hydrate; but this effect does not happen if the gypsum has been over-heated. It is often called Plaster of Paris. Artificial colored marbles, or *scagliola*, are frequently prepared by inserting pieces of natural stone in a soft stucco containing this substance, and polishing the surface when cement has become hard. Calcium sulphate is one of the most common impurities of spring water.

The peculiar property water acquires by the presence of calcium salts is termed *hardness.* It manifests itself by the effect such waters have upon the palate, and particularly by its peculiar behavior with soap. Hard water yields a lather with soap only after the whole of the calcium salts have been thrown down from the water in the form of an insoluble lime-soap. Upon this principle Prof. Clark's soap-test for the hardness of water is based.* The hardness produced by calcium sulphate is called *permanent hardness*, since it cannot be remedied.

Calcium Carbonate; Chalk; Limestone; Marble; CO_3Ca. — Calcium carbonate, often more or less contaminated with iron oxide, clay, and organic matter, forms rocky beds, of immense extent and thickness, in almost every part of the world. These present the greatest diversities of texture and appearance, arising, in a great measure, from changes to which they have been subjected since their deposition. The most ancient and highly

* Journal of the Pharmaceutical Society, vol. vi. p. 526.

crystalline limestones are destitute of visible organic remains, while those of more recent origin are often entirely made up of the shelly exuviæ of once-living beings. Sometimes these latter are of such a nature as to show that the animals inhabited fresh water; marine species and corals are, however, most abundant. Cavities in limestone and other rocks are very often lined with magnificent crystals of calcium carbonate or calcareous spar, which have evidently been slowly deposited from a watery solution. Calcium carbonate is always precipitated when an alkaline carbonate is mixed with a solution of that base.

Although this substance is not sensibly soluble in pure water, it is freely taken up when carbonic acid happens at the same time to be present. If a little lime-water be poured into a vessel of that gas, the turbidity first produced disappears on agitation, and a transparent solution of calcium carbonate in excess of carbonic acid is obtained. This solution is decomposed completely by boiling, the carbonic acid being expelled, and the carbonate precipitated. Since all natural waters contain dissolved carbonic acid, it is to be expected that calcium in this state should be of very common occurrence; and such is really found to be the fact, river, and more especially spring water, almost invariably containing calcium carbonate thus dissolved. In limestone districts, this is often the case to a great extent. The *hardness* of water, which is owing to the presence of calcium carbonate, is called *temporary*, since it is diminished to a very considerable extent by boiling, and may be nearly removed by mixing the hard water with lime-water, when both the dissolved carbonate and the dissolved lime, which thus becomes carbonated, are precipitated. Upon this principle Prof. Clark's process of softening water is based. This process is of considerable importance, since a supply of hard water to towns is in many respects a source of great inconvenience. As already mentioned, the use of such water, for the purposes of washing, is attended with a great loss of soap. Boilers, in which such water is heated, speedily become lined with a thick stony incrustation.* The beautiful stalactitic incrustations of limestone caverns, and the deposit of calc-sinter or travertin upon various objects, and upon the ground, in many places, are thus explained by the solubility of calcium carbonate in water containing carbonic acid.

Crystallized calcium carbonate is dimorphous; calc-spar and arragonite, although possessing exactly the same chemical composition, have different crystalline forms, different densities, and different optical properties. Rose has observed that calcium carbonate appears in the form of calc-spar when deposited from its solution in water containing carbonic acid at the ordinary temperature. At 90° C. (194° F.), and on ebullition, however, it is chiefly deposited in the form of arragonite; at lower temperatures the formation of arragonite decreases, whilst that of calc-spar increases, the limit for the formation of the former variety being between 30° and 50° C. (86°—122° F.).

Calc-spar occurs very abundantly in crystals derived from an obtuse rhombohedron, whose angles measure 105° 5′ and 74° 55′: its density varies from 2·5 to 2·8. The rarer variety, or arragonite, is found in crystals whose primary form is a right rhombic prism, a figure having no geometrical relation to the preceding: it is, besides, heavier and harder.

Calcium Phosphates. — A number of distinct calcium salts of phosphoric acid are known. The *tribasic phosphates*, or *orthophosphates*, $(PO_4)_2$

* Many proposals have been made to prevent the formation of boiler deposits. The most efficient appears to be the method of Dr. Ritterband, which consists in throwing into the boiler a small quantity of sal-ammoniac, when carbonate of ammonia is formed, which is volatilized with the steam, calcium chloride remaining in solution. It need scarcely be mentioned that this plan is inapplicable in the case of permanently hard waters.

Ca''_3 and $(PO_4)Ca''H$, are produced when the corresponding sodium salts are added in solution to calcium chloride; the first is slightly crystalline, and the second gelatinous. When the first phosphate is digested with ammonia, or dissolved in acid and re-precipitated by that alkali, it is converted into the second. The earth of bones consists principally of what appears to be a combination of these two salts. Another orthophosphate, $(PO_4)_2 Ca''H_4$, is formed by dissolving either of the preceding in phosphoric, hydrochloric, or nitric acid, and evaporating until the salt separates on cooling in small platy crystals. It is the substance which yields phosphorus when heated with charcoal, in the ordinary process of manufacture before described. *Pyrophosphates* and *Metaphosphates of calcium* also exist. These phosphates, although insoluble in water, dissolve readily in dilute acids, even in acetic acid. The mineral *apatite* is chiefly calcium phosphate.

Chloride of Lime; Bleaching Powder. — When calcium hydrate, very slightly moist, is exposed to chlorine gas, the latter is eagerly absorbed, and a compound produced which has attracted a great deal of attention: this is the bleaching powder of commerce, now manufactured on an immense scale, for bleaching linen and cotton goods. It is requisite, in preparing this substance, to avoid with the greatest care all elevation of temperature, which may be easily done by supplying the chlorine slowly in the first instance. The product, when freshly and well prepared, is a soft, white powder, which attracts moisture from the air, and exhales an odor sensibly different from that of chlorine. It is soluble in about 10 parts of water, the unaltered hydrate being left behind: the solution is highly alkaline, and bleaches feebly. When calcium hydrate is suspended in cold water, and chlorine gas transmitted through the mixture, the lime is gradually dissolved, and the same peculiar bleaching compound produced: the alkalies also, either caustic or carbonated, may by similar means be made to absorb a large quantity of chlorine, and give rise to corresponding compounds; such are the "disinfecting solutions" of Labarraque.

The most consistent view of the constitution of these compounds is that which supposes them to contain salts of hypochlorous acid, HClO, a substance as remarkable for bleaching powers as chlorine itself; and this opinion seems borne out by a careful comparison of the properties of the bleaching salts with those of the true hypochlorites. Hypochlorous acid can be actually obtained from good bleaching-powder, by distilling it with dilute sulphuric or nitric acid, in quantity insufficient to decompose the whole: when the acid is used in excess, chlorine is disengaged.*

If this view be correct, chloride of calcium must be formed simultaneously with the hypochlorite, as shown by the following equation:

$$\underset{\text{Lime.}}{2CaO} + Cl_4 = \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2} + \underset{\substack{\text{Calcium}\\\text{hypochlorite.}}}{CaCl_2O_2}$$

When the temperature of the calcium hydrate has risen during the absorption of the chlorine, or when the compound has been subsequently exposed to heat, its bleaching properties are impaired or altogether destroyed: it then contains chlorate and chloride of calcium; oxygen, in variable quantity, is usually set free. The same change seems to ensue by long keeping, even at the common temperature of the air. In an open vessel it is speedily destroyed by the carbonic acid of the air. Commercial bleaching-powder thus constantly varies in value with its age, and with the care originally bestowed upon its preparation: the best may contain about 30 per

* Gay-Lussac, Ann. Chim. Phys., 3d series, v. 296.

cent. of available chlorine, easily liberated by an acid, which is, however, far short of the theoretical quantity.

The general method in which this substance is employed for bleaching is the following: The goods are first immersed in a dilute solution of chloride of lime and then transferred to a vat containing dilute sulphuric acid. Decomposition ensues; the calcium both of the hypochlorite and of the chloride is converted into sulphate, while the free hypochlorous and hydrochloric acids yield water and free chlorine:

$$CaCl_2O_2 + CaCl_2 + 2SO_4H_2 = 2SO_4Ca + 2HClO + 2HCl;$$

and:

$$HClO + HCl = OH_2 + Cl_2.$$

The chlorine thus disengaged in contact with the cloth causes the destruction of the coloring matter. This process is often repeated, it being unsafe to use strong solutions. White patterns are on this principle imprinted upon colored cloth, the figures being stamped with tartaric acid thickened with gum-water, and then the stuff immersed in the chloride bath, when the parts to which no acid has been applied remain unaltered, while the printed portions are bleached.

For purifying an offensive or infectious atmosphere, *as an aid to proper ventilation*, the bleaching powder is very convenient. The solution is exposed in shallow vessels, or cloths steeped in it are suspended in the apartment, when the carbonic acid of the air slowly decomposes it in the manner above described. An addition of a strong acid causes rapid disengagement of chlorine.

The value of any sample of bleaching powder may be easily determined by the following method, in which the feebly combined chlorine is estimated by its effect in oxidizing a ferrous salt to ferric salt, 2 molecules of ferrous oxide, FeO, requiring for this purpose 2 atoms of chlorine: the latter acts by decomposing water and liberating a corresponding quantity of oxygen. 78 (more correctly 78·16) grains of green ferrous sulphate are dissolved in about two ounces of water, and acidulated by a few drops of sulphuric or hydrochloric acid: this quantity will require for oxidation 10 grains of chlorine. Fifty grains of the chloride of lime to be examined are next rubbed up with a little tepid water, and the whole transferred to the burette* before described, which is then filled up to 0 with water, after which the contents are well mixed by agitation. The liquid is next gradually poured into the solution of iron, with constant stirring, until all the iron is brought to the state of ferric salt, which may be known by a drop ceasing to give a deep-blue precipitate with potassium ferricyanide. The number of grain-measures of the chloride solution employed may then be read off: since these must contain 10 grains of serviceable chlorine, the quantity of the latter in the 50 grains may be easily reckoned. Thus, suppose 72 such measures have been taken; then

Measures.		Grs. Chlorine.		Measures.		Grs. Chlorine.
72	:	10	=	100	:	13·89

The bleaching-powder contains therefore 27·78 per cent.†

Calcium Sulphides. — The monosulphide, CaS, is obtained by reducing the sulphate at a high temperature with charcoal or hydrogen: it is nearly colorless, and but little soluble in water. By boiling together calcium hydrate, water, and flowers of sulphur, a red solution is obtained, which, on cooling, deposits crystals of the bisulphide, CaS_2, containing water.

* See p. 306.

† Graham's Elements, vol. i. p. 593. For other methods, see Watts's Dictionary of Chemistry, i. p. 904.

When the sulphur is in excess, and the boiling long continued, a pentasulphide is generated: hyposulphurous acid is formed as usual during these reactions.

Calcium Phosphide. — When vapor of phosphorus is passed over fragments of lime heated to redness in a porcelain crucible, a chocolate-brown compound, the so-called *phosphuret of lime*, is produced. This substance is probably a mixture of calcium phosphide and phosphate. When thrown into water it yields spontaneously inflammable hydrogen phosphide. According to Paul Thénard, the calcium phosphide in this compound has the composition P_2Ca_2. In contact with water it yields liquid hydrogen phosphide, P_2H_4 (p. 216):

$$P_2Ca_2 + 2OH_2 = 2CaO + P_2H_4:$$

and the greater portion of this liquid phosphide is immediately decomposed into solid and gaseous hydrogen phosphide:

$$\underset{\text{Liquid.}}{5P_2H_4} = \underset{\text{Solid.}}{P_4H_2} + \underset{\text{Gaseous.}}{6PH_3}$$

Reactions of the Alkaline Earth-metals in solution. — Barium, strontium, and calcium are thus distinguished from all other substances, and from each other.

Caustic *potash*, when free from carbonate, and caustic *ammonia*, occasion no precipitates in *dilute* solutions of the alkaline earths, especially of the first two, the hydrates being soluble in water.

Alkaline carbonates, and *carbonate of ammonia*, give white precipitates, insoluble in excess of the precipitant, with all three.

Sulphuric acid, or a *sulphate*, added to very dilute solutions of the salts of these metals, gives an immediate white precipitate with barium salts; a similar precipitate after a short interval with strontium salts; and occasions no change with calcium salts. The precipitates with barium and strontium salts are insoluble in nitric acid.

Solution of *calcium sulphate* gives an instantaneous cloud with barium salts, and one with strontium salts after a little time. *Strontium sulphate* is itself sufficiently soluble to occasion turbidity when mixed with barium chloride.

Lastly, the soluble *oxalates* give a white precipitate in the most dilute solutions of calcium salts, which is not dissolved by a drop or two of hydrochloric, or by an excess of acetic acid. This is an exceedingly characteristic test.

The *chlorides* of *strontium* and *calcium* dissolved in alcohol color the flame of the latter red or purple: *barium salts* communicate to the flame a pale green tint.

Silicofluoric acid gives a white precipitate with barium salts, none with salts of strontium or calcium.

GROUP II. — METALS OF THE EARTHS.

The dyad earth-metals are beryllium, thorinum, yttrium, erbium, lanthanum, and didymium. With these it will be convenient to describe the tetradic metals, aluminium, zirconum, and cerium; the first two because their oxides are of decidedly earthy character: in fact, alumina may be looked upon as the type of an earthy oxide; and the third on account of its constant association with lanthanum and didymium.

ALUMINIUM.

Atomic weight, 27·4. Symbol, Al.

This metal occurs very abundantly in nature in the state of silicate, as in felspar and its associated minerals; also in the various modifications of clay thence derived. It was first isolated by Wöhler, who obtained it as a gray powder by decomposing aluminium chloride with potassium; and H. Sainte-Claire Deville, by an improved process founded on the same principle, has succeeded in obtaining it in the compact form and on the manufacturing scale. The process consists in decomposing the double chloride of aluminium and sodium, Al_2Cl_6. 2NaCl, by heating it with metallic sodium, fluor-spar or cryolite being added as a flux. The reduction is effected in crucibles, or on the large scales on the hearth of a reverberatory furnace. Sodium is used as the reducing agent in preference to potassium: first, because it is more easily prepared; and, secondly, because it has a lower atomic weight, and, consequently, a smaller quantity of it suffices to do the same amount of chemical work.

Aluminium is also prepared directly from cryolite by reduction with sodium, but the metal thus obtained is said to be more contaminated with iron and silicium than that prepared by Deville's process.

Aluminium is remarkable for its low specific gravity, which is 2·6: it is nearly as white as silver, and is capable of assuming a high polish. It is employed in the manufacture of delicate apparatus and ornamental articles. Some of the alloys of aluminium promise to become more generally applicable, more especially the alloy with copper, which is remarkable for being similar in appearance to gold: this alloy is found already in commerce under the name of aluminium bronze.

Aluminium forms only one class of compounds, in all of which it appears to be trivalent, one atom of the metal being equivalent to three atoms of hydrogen; thus the chloride is Al'''_2Cl_6. the oxide Al'''_2O_3, &c. Each of these compounds, however, contains two atoms of aluminium, and it may therefore be supposed that the aluminium is really tetradic, one unit of equivalency in each atom being neutralized by one unit in the other; thus, the chloride is $\left|\begin{matrix}AlCl_3\\AlCl_3\end{matrix}\right.$. That such is the case is inferred from the resemblance of the aluminium compounds to the ferric and chromic compounds (p. 272).

Aluminium Chloride, Al_2Cl_6. — This compound is obtained in solution by dissolving alumina or aluminium hydrate in hydrochloric acid; but the solution, when evaporated, gives off hydrochloric acid and leaves alumina. The anhydrous chloride may be prepared by heating a mixture of alumina and finely divided carbon in chlorine gas.

Pure precipitated alumina is dried and mixed with oil and lampblack, and the mixture, after being strongly calcined in a covered crucible, is introduced into a porcelain tube or tubulated earthen retort placed in a furnace, and connected at one end with an apparatus for evolving chlorine, and at the other with a dry receiver. On raising the heat to bright redness, and passing chlorine through the apparatus, aluminium chloride distils over, together with carbon monoxide, and condenses as a solid mass in the receiver.

$$Al_2O_3 + C_3 + Cl_6 = Al_2Cl_6 + 3CO.$$

Aluminium chloride is a transparent waxy substance, having a crystal-

line structure, colorless when pure, but generally exhibiting a yellow color, due perhaps to the presence of iron. It boils at about 180°, fumes in the air, and smells of hydrochloric acid. It is very deliquescent, and dissolves readily in water; the solution when left to evaporate yields the hydrated chloride, $Al_2Cl_6.12OH_2$, in six-sided prisms, which when heated are resolved into alumina and hydrochloric acid.

Aluminium and Sodium Chloride, $Al_2Cl_6\ 2NaCl$, is obtained by melting together the component chlorides in proper proportions, or by adding the requisite quantity of sodium chloride to the mixture of alumina and charcoal used for the preparation of aluminium chloride, igniting the mass in chlorine or hydrochloric acid, and condensing the vapor in a receiver. It is a crystalline mass, less deliquescent than aluminium chloride, and, therefore, more convenient for the preparation of aluminium.

Aluminium Fluoride, Al_2F_6, is produced by the action of gaseous silicium fluoride on aluminium, and forms cubic crystals, volatilizing at a red heat, insoluble in water, and resisting the action of all acids.

Aluminium and Sodium Fluoride, $Al_2F_6.6NaF$, occurs abundantly, as cryolite, at Evigtok in Greenland, and is prepared artificially by pouring hydrofluoric acid in excess on a mixture of calcined alumina and sodium carbonate. Cryolite forms quadratic crystals, colorless, transparent, softer than felspar, and of specific gravity 2·96. It is used, as already mentioned, for the preparation of aluminium, and in Germany for the manufacture of soda for the use of soap-boilers.

Aluminium Oxide. Alumina, Al_2O_3. — This substance is inferred to be a sesquioxide from its isomorphism with ferric oxide. It is prepared by mixing a solution of alum with excess of ammonia, by which an extremely bulky, white, gelatinous precipitate of aluminium hydrate is thrown down. This is washed, dried, and ignited to whiteness. Thus obtained, alumina constitutes a white, tasteless, coherent mass, very little acted upon by acids. It is fusible before the oxy-hydrogen blowpipe. The mineral called *corundum*, of which the ruby and sapphire are transparent varieties, consists of nearly pure alumina in a crystallized state, with a little coloring oxide: emery, used for polishing glass and metals, is a coarse variety of corundum. Alumina is a very feeble base, and its salts have often an acid reaction.

Aluminium Hydrates. — Aluminium forms three hydrates; namely:

Monohydrate . .	$AlHO_2$	or $Al_2O_3 . OH_2$
Dihydrate . .	$Al_2H_4O_5$	or $Al_2O_3 . 2OH_2$
Trihidrate . .	$Al_2H_6O_6$	or $Al_2O_3 . 3OH_2$.

The monohydrate is found native, as *diaspore*, in translucent masses which crumble to powder when heated, and give off the whole of their water at 360°.

The *trihydrate* is the ordinary gelatinous precipitate obtained by treating solutions of aluminium-salts — alum, for example — with ammonia or alkaline carbonates. When dried at a moderate heat, it forms a soft friable mass, which adheres to the tongue and forms a stiff paste with water, but does not dissolve in that liquid. At a strong red heat, it parts with its water, and undergoes a very great contraction of volume. It dissolves with great facility in acids, and in the fixed caustic alkalies. When a solution of alumina in caustic potash is exposed to the air, the potash absorbs carbonic acid, and the aluminium trihydrate is then deposited in white crystals, which are but sparingly soluble in acids.

Aluminium trihydrate has a very powerful attraction for organic matter, and when digested in solutions of vegetable coloring-matter, combines with

and carries down the coloring matter, which is thus removed entirely from the liquid if the alumina is in sufficient quantity. The pigments called *lakes* are compounds of this nature. The fibre of cotton impregnated with alumina acquires the same power of retaining coloring matters: hence the great use of aluminous salts as *mordants* to produce fast colors.

Aluminium trihydrate occurs native as *Gibbsite*, a stalactitic, translucent, fibrous mineral, easily dissolved by acids.

Dihydrate. — When a dilute solution of aluminium diacetate is exposed for several days to a temperature of 100° in a close vessel, the acetic acid appears to be set free, although no precipitation of alumina takes place. The liquid acquires the taste of acetic acid, and if afterwards boiled in an open vessel, gives off nearly the whole of its acetic acid, the alumina nevertheless remaining in solution. This solution is coagulated by mineral acids and by most vegetable acids, by alkalies, and by decoctions of dye-woods. The alumina contained in it is, however, no longer capable of acting as a mordant. Its coagulum with dye-woods has the color of the infusion, but is translucent and totally different from the dense opaque lakes which ordinary alumina forms with the same coloring matters. On evaporating the solution to dryness at 100°, the alumina remains in the form of dihydrate, retaining only a trace of acetic acid. In this state it is insoluble in the stronger acids, but soluble in acetic acid, provided it has not been previously coagulated in the manner just mentioned. Boiling potash converts it into the trihydrate.*

Aluminates. — The hydrogen in aluminium trihydrate may be replaced by an equivalent quantity of various metals; such compounds are called *aluminates*. According to Frémy, a solution of alumina in potash slowly evaporated, out of contact with the air, deposits granular crystals of potassium aluminate, $Al'''KO_2$, or $Al_2O_3.OK_2$. Similar compounds occur native; thus *Spinell* is an aluminate of magnesium, $Al'''_2Mg''O_4$; *Gahnite*, an aluminate of zinc, $Al'''_2Zn''O_4$.

Aluminium Sulphide, Al_2S_3. — When the vapor of carbon bisulphide is passed over alumina, at a bright red-heat, a glassy melted mass remains, which is instantly decomposed by water, with evolution of sulphuretted hydrogen.

Aluminium Sulphate, $(SO_4)_3Al'''_2.18OH_2$, or $Al_2O_3.3SO_3.18OH_2$. — Prepared by saturating dilute sulphuric acid with aluminium hydrate, and evaporating; or, on the large scale, by heating clay with sulphuric acid. It crystallizes in thin pearly plates, soluble in 2 parts of water; it has a sweet and astringent taste, and an acid reaction. Heated to redness, it is decomposed, leaving pure alumina. Two other aluminium sulphates, with excess of base, are also described, one of which is insoluble in water.

Aluminium sulphate combines with the sulphates of potassium, sodium, and ammonium, and the other alkali-metals, forming double salts of great interest, the *alums*. Common alum, the source of all the preparations of alumina, contains $(SO_4)_2Al'''K.12OH_2$. It is manufactured on a very large scale from a kind of slaty clay, loaded with iron bisulphide, which abounds in certain localities. This is gently roasted, and then exposed to the air in a moistened state; oxygen is absorbed; the sulphur becomes acidified; ferrous sulphate and aluminium sulphate are produced, and afterwards separated by lixiviation with water. The solution is next concentrated, and mixed with a quantity of potassium chloride, which decomposes the iron-salt, forming ferrous chloride and potassium sulphate: the latter combines with the aluminium sulphate to form alum. By crystallization the alum is

* Walter Crum, Chem. Soc. Journ. vi. 225.

separated from the highly soluble iron chloride, and afterwards easily purified by a repetition of the process. Other methods of alum-making exist, and are sometimes employed. Potassium-alum crystallizes in colorless, transparent octohedrons which often exhibit the faces of the cube. It has a sweetish and astringent taste, reddens litmus-paper, and dissolves in 18 parts of water at 15·5°, and in its own weight of boiling water. Exposed to heat, it is easily rendered anhydrous, and by a very high temperature it is decomposed. The crystals have little tendency to change in the air. Alum is largely used in the arts, in preparing skins, dyeing, &c.: it is occasionally contaminated with iron oxide, which interferes with some of its applications. The celebrated Roman alum, made from *alum-stone*, a felspathick rock altered by sulphurous vapors, was once much prized on account of its freedom from this impurity. A mixture of dried alum and sugar, carbonized in an open pan, and then heated to redness in a glass flask, contact with air being avoided, furnishes the *pyrophorus of Homberg*, which ignites spontaneously on exposure to the atmosphere. The essential ingredient is, in all probability, finely divided potassium sulphide.

Sodium-alum, in which sulphate of sodium replaces sulphate of potassium, has a form and constitution similar to that of the salt described: it is, however, much more soluble, and difficult to crystallize.

Ammonium-alum, containing NH_4 instead of K, very closely resembles common potassium-alum, having the same figure, appearance, and constitution, and nearly the same degree of solubility as that substance. It is manufactured for commercial use. As the value of potassium salts is continually increasing, ammonium-alum, which may be used in dyeing with the same advantage as the corresponding potassium salt, has almost entirely replaced the potassium-alum. When heated to redness, ammonium-alum yields pure alumina.

Cæsium-alum, $(SO_4)_2Al'''Cs.12OH_2$, and *Rubidium-alum*, $(SO_4)_2Al'''Rb.12OH_2$, resemble potassium alum. A *silver alum*, $(SO_4)_2Al'''Ag.12OH_2$, is formed by heating equivalent quantities of argentic and aluminium sulphates till the former is dissolved. It crystallizes in regular octohedrons, and is resolved by water into its component salts. There is also a *thallium alum*, $(SO_4)_2Al'''Tl.12OH_2$, which crystallizes in regular octohedrons.

Lastly, there are alums isomorphous with those just described, in which the trivalent aluminium is replaced by trivalent iron, chromium, and manganese: for example, potassio-ferric sulphate or potassium iron alum, $(SO_4)_2Fe'''K.12OH_2$; *ammonio-chromic sulphate*, $(SO_4)_2Cr'''NH_4.12OH_2$. These will be described further on.

Few other aluminium salts present especial interest, except the silicates; but these latter are of great importance. Silicates of aluminium enter into the composition of a number of crystallized minerals, among which felspar, by reason of its abundant occurrence, occupies a prominent place. Granite, porphyry, trachyte, and other ancient unstratified rocks, consist in great part of this mineral, which, under peculiar circumstances by no means well understood, and particularly by the action of the carbonic acid of the air, suffer complete decomposition, becoming converted into a soft, friable mass of earthy matter. This is the origin of clay; the change itself is seen in great perfection in certain districts in Devonshire and Cornwall, the felspar of the fine white granite of those localities being often disintegrated to an extraordinary depth, and the rock altered to a substance resembling soft mortar. By washing, this finely divided matter is separated from the quartz and mica; and the milk-like liquid, being collected in tanks and suffered to stand, deposits the suspended clay, which is afterwards dried, first in the air, and afterwards in a stove, and employed in the manufacture of porcelain. The composition assigned to unaltered felspar is Si_3O_8AlK, or $SiO_4AlK.2SiO_2$, or $6SiO_2.Al_2O_3.K_2O$. The exact nature

of the change by which felspar passes into porcelain clay is unknown, although it evidently consists in the abstraction of silica and alkali.

When the decomposing rock contains iron oxide, the clay produced is colored. The different varieties of shale and slate result from the alteration of ancient clay-beds, apparently in many instances by the infiltration of water holding silica in solution: the dark appearance of some of these deposits is due to bituminous matter.

It is a common mistake to confound clay with alumina: all clays are essentially silicates of that base; they often vary a good deal in composition. Dilute acids exert little action on these compounds; but by boiling with oil of vitriol, alumina is dissolved out, and finely divided silica left behind. Clays containing an admixture of calcium carbonate are termed *marls*, and are recognized by effervescing with acids.

A basic aluminium silicate, $Al_2O_3.SiO_2$, is found crystallized, constituting the beautiful mineral called *cyanite*. The compounds formed by the union of the aluminium silicates with other silicates are almost innumerable. A sodium felspar, *albite*, containing that metal in place of potassium, is known, and there are two somewhat similar lithium-compounds, *spodumene* and *petalite*. The *zeolites* belong to this class; *analcime*, *nepheline*, *mesotype*, &c., are double silicates of sodium and aluminium, with water of crystallization. *Stilbite*, *heulandite*, *laumontite*, *prehnite*, &c., consist of calcium silicate combined with silicate of aluminium. The *garnets*, *axinite*, *mica*, &c., have a similar composition, but are anhydrous. Iron sesquioxide is very often substituted for alumina in these minerals.

Salts of aluminium, when moistened with *cobalt nitrate* and heated before the blowpipe, assume a characteristic blue color.

Alumina, when in solution, is distinguished without difficulty. Caustic *potash* and *soda* occasion white gelatinous precipitates of aluminium hydrate, freely soluble in excess of the alkali. *Ammonia* produces a similar precipitate, insoluble in excess of the reagent. The *alkaline carbonates* and *carbonate of ammonia* precipitate the hydrate, with escape of carbonic acid. The precipitates are insoluble in excess.

Ammonium sulphide also produces a white precipitate of aluminium hydrate.

BERYLLIUM, or GLUCINUM.

Atomic weight, 9·4. Symbol, Be.

This somewhat rare metal occurs as a silicate, either alone, as in phenacite, or associated with other silicates, as beryl, euclase, leucophane, helvite, and several varieties of gadolinite; also as an aluminate in chrysoberyl or cymophane.

Metallic beryllium is obtained by passing the vapor of the chloride over melted sodium. It is a white metal of specific gravity 2·1; it may be forged and rolled into sheets like gold; its melting point is below that of silver. It does not decompose water at the boiling heat. Sulphuric and hydrochloric acids dissolve it, with evolution of hydrogen.

Beryllium forms but one class of compounds, and there is considerable doubt as to its atomic weight and equivalent value. On the one hand it is regarded as a dyad, like calcium and magnesium, with the atomic weight 9·4, its chloride being $BeCl_2$, its oxide BeO; on the other hand, as a tetrad, like aluminium, with apparent tri-equivalent value, on which supposition its chloride would be Be_2Cl_6, its oxide Be_2O_3, and its atomic weight 14; but

the former view appears, on the whole, to be most in accordance with observed facts.

Beryllium Chloride, $BeCl_2$, is formed by heating the metal in chlorine or hydrochloric acid gas, or by the action of aqueous hydrochloric acid on the metal or its oxide.

The anhydrous chloride is prepared by passing chlorine over an ignited mixture of beryllia and charcoal. It is less volatile than aluminium chloride, very deliquescent, and easily soluble in water.

Beryllium Oxide. Beryllia, BeO. — This earth may be prepared from beryl, or either of the other beryllium silicates, by fusing the finely pounded mineral with potassium carbonate or quicklime; treating the fused mass with hydrochloric acid; evaporating to dryness; then moistening the residue with hydrochloric acid, and treating it with water, whereby everything is dissolved except the silica. The filtered liquid is then mixed with excess of ammonia solution, which throws down a bulky precipitate containing both alumina and beryllia; this precipitate is well washed, and the beryllia is dissolved out from the alumina by digestion in a cold strong solution of ammonium carbonate. The liquid is again filtered, and on boiling it, beryllium carbonate is deposited as a white powder, which, when ignited, leaves pure beryllia.

Beryllia is very much like alumina in physical characters, and further resembles that substance in being readily dissolved by caustic potash or soda; but it is distinguished from alumina by its solubility, when recently precipitated, in a cold solution of ammonium carbonate.

Beryllium salts have a sweet taste, whence the former name of the metal, *glucinum* (from γλυκύς). They are colorless, and are distinguished from those of aluminium by not yielding an alum with potassium sulphate, nor a blue color when heated before the blowpipe with cobalt nitrate; also by their reaction with ammonium carbonate.

ZIRCONIUM.

Atomic weight, 89·6. Symbol, Zr.

This is a tetrad metal, intermediate in many of its properties between aluminium and silicium. Its oxide, zirconia, was first obtained by Klaproth, in 1789, from zircon, which is a silicate of zirconium. It has since been found in fergusonite, eudialyte, and two or three other rare minerals.

Zirconium, like silicium, is capable of existing in three different states, amorphous, crystalline, and graphitoïdal. The amorphous and crystalline varieties are obtained by processes similar to those described for preparing the corresponding modifications of silicium; graphitoïdal zirconium was obtained, by Troost, in attempting to decompose sodium zirconate with iron, in light scales of a steel-gray color. Amorphous zirconium when heated in the air takes fire at a heat somewhat below redness, and burns with a bright light, forming zirconia. Crystalline zirconium forms very hard brittle scales resembling antimony in color and lustre; it burns in the air only at the heat of the oxy-hydrogen blowpipe, but takes fire at a red heat in chlorine gas. Zirconium is but little attacked by the ordinary acids; but hydrofluoric acid dissolves it readily, with evolution of hydrogen.

Zirconium Oxide, or Zirconia, ZrO_2, is prepared by strongly igniting zircon (zirconium silicate) with four times its weight of dry sodium carbonate and a small quantity of sodium hydrate. The silica is separated from

the fused mass by hydrochloric acid, as described in the case of beryllia; the resulting solution is treated with ammonia, which throws down zirconia generally mixed with ferric oxide; the precipitate is redissolved in hydrochloric acid; and the solution is boiled with excess of sodium hyposulphite as long as sulphurous acid continues to escape, whereby pure zirconia is precipitated, the whole of the iron remaining in the solution. Zirconia thus obtained forms a white powder or hard lumps of specific gravity 4·35 to 4·9. By fusing it with borax in a pottery furnace and dissolving out the soluble salts with hydrochloric acid, zirconia is obtained in small quadratic prisms, isomorphous with the native oxides of tin and titanium.

Zirconium hydrates are obtained by precipitating the solution of a zirconium salt with ammonia; the precipitate contains $ZrH_2O_3 = ZrO_2.OH_2$, or $ZrH_4O_4 = ZrO_2.2OH_2$, according to the temperature at which it is dried.

Zirconia acts both as a base and as an acid. After ignition it is insoluble in all acids except hydrofluoric and very strong sulphuric acid; but the hydrate dissolves easily in acids, forming the zirconium salts; the normal sulphate has the composition $(SO_4)_2Zr^{iv}$, or $SO_3.ZrO_2$.

Compounds of zirconia with the stronger bases, called *zirconates*, are obtained by precipitating a zirconium salt with potash or soda, or by igniting zirconia with an alkaline hydrate. *Potassium zirconate* dissolves completely in water. Three *sodium zirconates* have been formed, containing $ZrO_3Na_2 = ZrO_2.ONa_2$; $ZrO_4Na_4 = ZrO_2.2ONa_2$; and $Zr_8O_{17}Na_2 = 8ZrO_2.ONa_2$.

Zirconium Fluoride, ZrF_4. — This compound is obtained by dissolving zirconia, or the hydrate, in hydrofluoric acid; or in the anhydrous state, by igniting zirconia with ammonium and hydrogen fluoride (p. 276) till all the ammonium fluoride is driven off. It unites with other metallic fluorides, forming double salts, called *zircofluorides* or *fluozirconates*, which are isomorphous with the corresponding silicofluorides, stannofluorides, and titanofluorides, and are mostly represented by the formulæ

$$4MF.ZrF_4; \quad 3MF.ZrF_4; \quad 2MF.ZrF_4; \quad MF.ZrF_4,$$

in which M denotes a monad metal. The sodium salt, however, has the composition $5NaF.3ZrF_4$.

THORINUM, or THORIUM.

Atomic weight, 115·75. Symbol, Th.

This very rare metal was discovered in 1828 by Berzelius, in thorite, a mineral from the Norwegian island Lovön, in which it exists as a silicate. It has since been found in euxenite, pyrochlore, and a few other minerals, all very scarce.

Metallic thorinum is obtained by reducing the chloride with potassium or sodium, as a gray powder, which acquires metallic lustre by pressure, and has a density of 7·66 to 7·9. It is not oxidized by water, dissolves easily in nitric, slowly in hydrochloric acid, and is not attacked by caustic alkalies.

Thorinum forms but one class of compounds, in all of which it is bivalent.

Thorinum Oxide, or Thorina, ThO, is prepared by decomposing thorite with hydrochloric acid, separating the silica in the usual way, treating the filtered solution with hydrogen sulphide to separate lead and tin, and precipitating the thorina by ammonia, together with small quantities of the oxides of iron, manganese, and uranium. To get rid of these, the precipitate is redissolved in hydrochloric acid, and the hot saturated solution is boiled with a solution of neutral potassium sulphate. The thorinum is

thereby precipitated as thorinum and potassium sulphate; and from the solution of this salt in hot water, the thorinum is precipitated as a hydrate, which, on ignition, yields pure thorina.

Thorina is white, and very heavy, its specific gravity being 9.402. After ignition it is insoluble in nitric and hydrochloric acids, and dissolves in strong sulphuric acid only after prolonged heating. The *hydrate* precipitated from thorinum salts by alkalies dissolves easily in acids.

Thorinum Chloride, $ThCl_2$, prepared by igniting an intimate mixture of thorina and charcoal in chlorine gas, sublimes in white shining crystals. It forms double salts with the chlorides of the alkali-metals.

Thorinum Sulphate, SO_4Th'', crystallizes with various quantities of water, according to the temperature at which its solution is evaporated. *Thorinum and potassium sulphate*, $(SO_4)_2Th''K_2 . OH_2$, separates as a crystalline powder when a crust of potassium sulphate is suspended in a solution of thorinum sulphate. It is easily soluble in water, but insoluble in alcohol and in solution of potassium sulphate.

CERIUM. — LANTHANUM. — DIDYMIUM.

Ce = 92. — La = 92·8. — Di = 96.

These three metals occur together as silicates in the Swedish mineral cerite, also in allanite, orthite, and a few others; and as phosphates in monazite, edwardsite, and cryptolite, a mineral occurring disseminated through apatite and through certain cobalt ores.

Cerium was discovered in 1803 by Klaproth, and by Hisinger and Berzelius, who obtained it in the form of oxide from cerite. This mineral is completely decomposed by boiling with strong hydrochloric acid, silica being separated, and the cerium, together with iron and other metals, dissolving as chloride. On treating the acid solution thus obtained with oxalic acid, cerium oxalate is precipitated as a white crystalline powder, which, when ignited, leaves a brown oxide. The product thus obtained was for some time regarded as the oxide of a single metal, *cerium;* but in 1839 and 1841, Mosander* showed that it contained the oxides of two other metals, which he designated as *lanthanum*† and *didymium*.‡

Cerium oxide may be separated from the oxides of lanthanum and didymium by treating the crude brown oxide above mentioned, first with dilute and then with strong nitric acid, which gradually removes the whole of the lanthanum and didymium oxides.

The separation of these two oxides one from the other is much more difficult, and can be effected only by successive crystallization of their sulphates. If the lanthanum salt is in excess, in which case the solution of the mixed sulphates has only a faint amethyst tinge, the liquid is evaporated to dryness, and the residue heated to a temperature just below redness, to render the sulphates anhydrous. The residue thus obtained is then to be added by small portions to ice-cold water, in which it dissolves easily, and the resulting solution heated in a water-bath to about 40°. Lanthanum sulphate then crystallizes out, containing only a small quantity of didymium, and may be further purified by repeating the whole process. If, on the other hand, the didymium salt is in excess, in which case the liquid has a

* Poggendorff's Annalen, xlvi. 648; xlvii. 207; lvi. 504.

† From λανθάνειν, to lie hid.

‡ From δίδυμοι, twins.

decided rose color, separation may be effected by leaving the acid solution in a warm place for a day or two. Didymium sulphate then separates in large rhombohedral crystals.

Metallic cerium, lanthanum, and didymium are obtained by reducing the chlorides with sodium, in the form of gray powders, which decompose water at ordinary temperatures, and dissolve rapidly in dilute acids with evolution of hydrogen.

Cerium forms *three* series of compounds: the *cerous compounds*, in which it is bivalent, *e. g.*, $CeCl_2$, CeO, $CeSO_4$; the *ceric compounds*, in which it is apparently trivalent, but really quadrivalent, like the ferric salt, *e. g.*, ceric fluoride, $Ce_2F_6 = \begin{matrix} CeF_3 \\ | \\ CeF_3 \end{matrix}$; and the *ceroso-ceric compounds*, of intermediate composition, and, perhaps, consisting of compounds of the other two, *e. g.*, ceroso-ceric oxide, $Ce_3O_4 = CeO.Ce_2O_3$.

Cerous oxide, CeO, is obtained by igniting the carbonate or oxalate in a current of hydrogen, as a grayish-blue powder, quickly converted into ceroso-ceric oxide on exposure to the air. Its salts are colorless. The *sulphate*, SO_4Ce, crystallizes with various quantities of water, according to the temperature at which it is deposited. *Cerium* and *potassium sulphate*, $(SO_4)_2CeK_2$, separates as a white powder on immersing solid potassium sulphate in a solution of a cerous salt. It is slightly soluble in pure water, but insoluble in a saturated solution of potassium sulphate. The formation of this salt affords the means of separating cerium from most other metals.

The only ceric compounds actually known are the *fluoride*, Ce_2F_6, already mentioned, which may be obtained as a yellow precipitate, and likewise occurs native as *fluocerite*, and an oxyfluoride, $Ce_4F_6O_3$, occurring as *fluocerine* at Finnbo, in Sweden.

Ceroso-ceric oxide,* Ce_3O_4, or $\begin{matrix} O = Ce \\ | \quad > O \\ Ce \\ | \quad > O \\ O = Ce \end{matrix}$, analogous in composition to ferrosoferric or magnetic iron oxide, is produced when cerous hydrate, carbonate, or nitrate is ignited in an open vessel. It is yellowish-white, acquires a deep orange-red color when heated, but recovers its original tint on cooling. It is not converted into a higher order by ignition in hydrogen. *Ceroso-ceric hydrate*, $Ce_3O_4 . 3OH_2$, obtained by passing chlorine into aqueous potash in which cerous hydrate is suspended, is a bright-yellow precipitate, which dissolves readily in sulphuric and nitric acids, forming yellow solutions of ceroso-ceric salts; and in hydrochloric acid, with evolution of chlorine, forming colorless cerous chloride.

The solution of the sulphate yields by spontaneous evaporation, first, brown-red crystals of the salt, $(SO_4)_6Ce_5 . 18$ aq., or $3SO_4Ce''. (SO_4)_3Ce'''_2 . 18$ aq., and afterwards a yellow indistinctly crystalline salt, containing $SO_4Ce''. (SO_4)_3Ce'''_2 . 18$ aq.†

All ceroso-ceric compounds, when heated with hydrochloric acid, give off chlorine, and are reduced to the corresponding cerous compounds; thus:

$$\underset{\text{Ceroso-ceric oxide.}}{Ce_3O_4} + 8HCl = \underset{\text{Cerous chloride.}}{3CeCl_2} + 4OH_2 + Cl_2.$$

* A sesquioxide, Ce_2O_3, is commonly said to exist, and is designated as ceric oxide, but there is no proof of its existence; neither are any salts of analogous composition known with certainty.

† The symbol aq. (abbreviation of *aqua*) is often used to denote water of crystallization.

Lanthanum is bivalent, forming only one set of compounds, viz. $LaCl_2$, LaO, $LaSO_4$. There is, however, a higher oxide, the composition of which is not exactly known. Lanthanum salts are colorless; their solutions yield, with alkalies, a precipitate of *lanthanum hydrate*, LaH_2O_2, or $LaO.OH_2$, which, when ignited, leaves the white anhydrous monoxide. Both the hydrate and the anhydrous oxide dissolve easily in acids. *Lanthanum sulphate* forms small prismatic crystals, containing $SO_4La.3OH_2$. *Lanthanum* and *potassium sulphate*, $(SO_4)_2LaK_2$, is formed, on mixing the solution of a lanthanum salt with potassium sulphate, as a white crystalline precipitate, resembling the corresponding cerium salt.

Didymium is also bivalent; its salts are rose-colored, and their solutions give, with alkalies, a pale rose-colored precipitate of the *hydrate*, DiH_2O_2, which, when ignited in a covered crucible, leaves the anhydrous monoxide, DiO, in white, hard lumps. When, however, the hydrate, nitrate, carbonate, or oxalate of didymium is heated in contact with the air, and not very strongly, a dark-brown peroxide is left, containing from 0·8 to 0·9 per cent. oxygen more than the monoxide. This, when treated with acids, dissolves readily, giving off oxygen and yielding a salt of the monoxide.

Didymium sulphate separates from an acid solution, by spontaneous evaporation, in well-defined rhombohedral crystals, exhibiting numerous secondary faces, and containing $3SO_4Di.8$ aq.: they are isomorphous with the similarly constituted sulphates of yttrium, erbium, and cadmium. The sulphate is more soluble in cold than in hot water, and a solution saturated in the cold deposits, when heated to the boiling-point, a crystalline powder containing $SO_4Di \cdot 2$ aq.

Didymium and *potassium sulphate*, $(SO_4)_2DiK_2$, resembles the lanthanum salt.

Solutions of didymium salts exhibit a well-marked absorption spectrum,* containing two black lines inclosing a very bright space. One of these black lines is in the yellow, immediately following Fraunhofer's line D; the other is situated between E and *b*. These characters can be distinctly recognized in a solution half an inch deep, containing only 0·01 per cent. of didymium salt. Lanthanum salts do not exhibit an absorption spectrum (Gladstone).

YTTRIUM AND ERBIUM.

$Y = 61{\cdot}7$. $Eb = 112{\cdot}6$.

These metals exist as silicates in the gadolinite or ytterbite of Ytterby in Sweden, and in a few other rare minerals. A third metal, called terbium, has also been supposed to be associated with them; but recent experiments, especially those of Bahr and Bunsen,† have thrown very great doubt upon its existence.

To obtain the earths, yttria and erbia, in the separate state, gadolinite is digested with hydrochloric acid, and the solution separated from the silica is treated with oxalic acid, which throws down the oxalates of erbium and yttrium, together with those of calcium, cerium, lanthanum, and didymium. These oxalates are converted into nitrates; the solution is treated with excess of solid potassium sulphate, to separate the cerium metals; the erbium and yttrium, which still remain in solution, are again precipitated by oxalic acid; and the same treatment is repeated, till the solution of the mixed earths, when examined by the spectral apparatus, no longer exhibits the absorption bands characteristic of didymium. To separate

* See LIGHT, p. 90.

† Ann. Ch. Pharm. cxxxvii. 1.

the erbia and yttria, they are again precipitated by oxalic acid. The oxalates are converted into nitrates, and the nitrates of erbium and yttrium are separated by a series of fractional crystallizations, the erbium salt being the less soluble of the two, and crystallizing out first; but the process requires attention to a number of details, which cannot be here described.*

Metallic erbium has not been isolated. Yttrium (containing erbium) was obtained by Berzelius, as a blackish-gray powder, by igniting yttrium chloride with potassium.

Erbia, $Eb''O$, obtained by ignition of erbium nitrate or oxalate, has a faint rose color. It does not melt at the strongest white heat, but aggregates to a spongy mass, glowing with an intense *green* light, which, when examined by the spectroscope, exhibits a *continuous* spectrum intersected by a number of bright bands. Solutions of erbium-salts, on the other hand, give an absorption-spectrum exhibiting dark bands, and *the points of maximum intensity of the light bands in the emission-spectrum of glowing erbia coincide exactly in position with the points of greatest darkness in the absorption-spectrum.* The position of these bands is totally different from those in the emission and absorption-spectra of didymium.†

Erbium salts have a rose-red color, deeper in the hydrated than in the anhydrous state; they have an acid reaction and sweet astringent taste. The *sulphate*, $3SO_4Eb'' . 8aq.$, forms light rose-colored crystals, isomorphous with the sulphates of yttrium and didymium.

Yttria, $Y''O$, is a soft, nearly white powder, which when ignited glows with a pure white light, and yields a spectrum not containing any bright bands, like that of erbia. It does not unite directly with water, but is precipitated as a hydrate by alkalies, from solutions of yttrium-salts. It dissolves slowly but completely in hydrochloric, nitric, and sulphuric acids, forming colorless solutions, which do not exhibit an absorption-spectrum.

Yttrium sulphate, $3SO_4Y'' . 8aq.$, forms small colorless crystals.

Reactions of the Earth-Metals.

1. All these metals are precipitated from their solutions by ammonium sulphide, as hydrates, not as sulphides. They are not precipitated by hydrogen sulphide.

2. The hydrates of aluminium and beryllium are soluble in *caustic potash;* those of the other earth-metals are insoluble.

3. Beryllium hydrate dissolves in a cold saturated solution of *ammonium carbonate*, and is precipitated, as carbonate, on boiling. Aluminium hydrate is insoluble in ammonium carbonate (see further, p. 337).

4. Of the earth-metals whose hydrates are insoluble in potash, — namely, zirconium, thorinum, cerium, lanthanum, didymium, erbium, and yttrium, — zirconium and thorinum may be precipitated as hyposulphites by boiling the solution with *sodium hyposulphite*, the other metals remaining in solution. The precipitate when ignited leaves pure zirconia or thorina, or a mixture of the two.

5. Zirconium and thorinum may be separated one from the other by means of *ammonium oxalate*, which, when added in excess, precipitates the thorinum as oxalate, and leaves the zirconium in solution.

6. Cerium, lanthanum, and didymium are separated from yttrium and erbium by adding an excess of *potassium sulphate*, which throws down the

* See Watts's Dictionary of Chemistry, vol v. p. 721.

† The paper by Bahr and Bunsen, above referred to, is accompanied by exact diagrams of the erbium and didymium spectra.

cerium metals, leaving yttrium and erbium in solution; to insure complete precipitation, the solution must be left in contact for some time with a piece of solid potassium sulphate

Cerium may be separated from lanthanum and didymium, as already observed, by treating the mixed oxides several times with *nitric acid* (p. 340). Another method is to boil the mixed oxides (the cerium being in the state of ceroso-ceric oxide) with solution of *sal-ammoniac*. The lanthanum and didymium then gradually dissolve, as chlorides, while the cerium remains as ceroso-ceric oxide. A third method is to precipitate the solution of the three metals with excess of potash, and pass *chlorine* in excess through the solution and precipitate; the cerium is then separated as bright-yellow ceroso-ceric hydrate, while the lanthanum and didymium redissolve as chlorides. This reaction serves to detect very small quantities of cerium mixed with the other two metals. Cerium is further distinguished by the light-yellow color of anhydrous ceroso-ceric oxide, and by the reaction of its compounds when fused before the blow-pipe with borax or phosphorus salt, the glass thus formed being deep-red while hot, and becoming colorless on cooling. Didymium is distinguished by the dark-brown color of its higher oxide; by the pale rose-color which its salts impart to a bead of borax or phosphorus salt; and by the peculiar character of its absorption spectrum (p. 342).

The methods of separating lanthanum from didymium, and yttrium from erbium — imperfect at the best — have been already noticed.

MANUFACTURE OF GLASS, PORCELAIN, AND EARTHENWARE.

Glass. — Glass is a mixture of various insoluble silicates with excess of silica, altogether destitute of crystalline structure; the simple silicates, formed by fusing the bases with silicic acid in equivalent proportions, very often crystallize, which happens also with the greater number of the natural silicates included among the earthy minerals. Compounds identical with some of these are also occasionally formed in artificial processes, where large masses of melted glassy matter are suffered to cool slowly. The alkaline silicates, when in a state of fusion, have the power of dissolving a large quantity of silica.

Two principal varieties of glass are met with in commerce — namely, glass composed of silica, alkali, and lime, and glass containing a large proportion of lead silicate; *crown* and *plate glass* belong to the former division; *flint glass*, and the material of artificial gems, to the latter. The lead promotes fusibility, and confers also density and lustre. Common green bottle-glass contains no lead, but much silicate of iron, derived from the impure materials. The principle of the glass manufacture is very simple. Silica, in the shape of sand, is heated with potassium or sodium carbonate, and slaked lime or lead oxide; at a high temperature, fusion and combination occur, and the carbonic acid is expelled. Glauber's salt mixed with charcoal is sometimes substituted for soda. When the melted mass has become perfectly clear and free from air-bubbles, it is left to cool until it assumes the peculiar tenacious condition proper for working.

The operation of fusion is conducted in large crucibles of refractory fire-clay, which in the case of lead-glass are covered by a dome at the top, and have an opening at the side, by which the materials are introduced, and the melted glass withdrawn. Great care is exercised in the choice of the sand, which must be quite white and free from iron oxide. Red lead, one of the higher oxides, is preferred to litharge, although immediately reduced to monoxide by the heat, the liberated oxygen serving to destroy any combustible matter that might accidentally find its way into the crucible, and stain the glass by reducing a portion of the lead. Potash gives a better

glass than soda, although the latter is very generally employed, from its lower price. A certain proportion of broken and waste glass of the same kind is always added to the other materials.

Articles of blown glass are thus made: The workman begins by collecting a proper quantity of soft pasty glass at the end of his *blowpipe*, an iron tube five or six feet in length, terminated by a mouthpiece of wood; he then begins blowing, by which the lump is expanded into a kind of flask, susceptible of having its form modified by the position in which it is held, and the velocity of rotation continually given to the iron tube. If an open-mouthed vessel is to be made, an iron rod, called a *pontil* or *puntil*, is dipped into the glass pot and applied to the bottom of the flask, to which it thus serves as a handle, the blowpipe being removed by the application of a cold iron to the neck. The vessel is then re-heated at a hole left for the purpose in the wall of the furnace, and the aperture enlarged, and the vessel otherwise altered in figure by the aid of a few simple tools, until completed. It is then detached, and carried to the annealing oven, where it undergoes slow and gradual cooling during many hours, the object of which is to obviate the excessive brittleness always exhibited by glass which has been quickly cooled. The large circular *tables* of crown glass are made by a very curious process of this kind: the globular flask at first produced, transferred from the blowpipe to the pontil, is suddenly made to assume the form of a flat disc by the centrifugal force of the rapid rotatory movement given to the rod. Plate glass is cast upon a flat metal table, and, after very careful annealing, ground true and polished by suitable machinery. Tubes are made by rapidly drawing out a hollow cylinder; and from these a great variety of useful small apparatus may be constructed with the help of a lamp and blowpipe, or, still better, the bellows-table of the barometer-maker. Small tubes may be bent in the flame of a spirit-lamp or gas jet, and cut with great ease by a file, a scratch being made, and the two portions pulled or broken asunder in a way easily learned by a few trials.

Specimens of the two chief varieties of glass gave the following results on analysis:

Bohemian plate glass (excellent).*		English flint glass.†	
Silica	60·0	Silica	51·93
Potassium oxide	25·0	Potassium oxide	13·77
Lime	12·5	Lead oxide	33·28
	97·5		98·98

The difficultly fusible white Bohemian tube, so valuable in organic analysis, has been found to contain, in 100 parts:

Silica	72·80
Lime, with trace of alumina	9·68
Magnesia	·40
Potassium oxide	16·80
Traces of manganese, &c., and loss	·32

Different colors are often communicated to glass by metallic oxides. Thus, oxide of cobalt gives deep blue; oxide of manganese, amethyst; cuprous oxide, ruby-red; cupric oxide, green; the oxides of iron, dull green or brown, &c. These are either added to the melted contents of the glass-pot, in which they dissolve, or applied in a particular manner to the surface of the plate or other object, which is then reheated, until fusion of the coloring matter occurs: such is the practice of enamelling and glass-paint-

* Mitscherlich, Lehrbuch, ii. 187. † Faraday.

ing. An opaque white appearance is given by oxide of tin; the enamel of watch-faces is thus prepared.

When silica is melted with twice its weight of potassium or sodium carbonate, and the product treated with water, the greater part dissolves, yielding a solution from which acids precipitate gelatinous silica. This is the *soluble glass* of Professor Fuchs: its solution has been used for rendering muslin and other fabrics of cotton or linen less combustible, for making artificial stone, and preserving natural stone from decay, and for a peculiar style of mural painting called *stereochromy*.*

Porcelain and Earthenware. — The plasticity of natural clays, and their hardening when exposed to heat, are properties which suggested in very early times their application to the making of vessels for the various purposes of daily life: there are few branches of industry of higher antiquity than that exercised by the potter.

True porcelain is distinguished from earthenware by very obvious characters. In porcelain the *body* of the ware is very compact and translucent, and breaks with a conchoïdal fracture, symptomatic of a commencement of fusion. The glaze, too, applied for giving a perfectly smooth surface, is closely adherent, and, in fact, graduates by insensible degrees into the substance of the body. In earthenware, on the contrary, the fracture is open and earthy, and the glaze detachable with greater or less facility. The compact and partly glassy character of porcelain is the result of the admixture with the clay of a small portion of some substance which is fusible at the temperature to which the ware is exposed when baked or fired, and being absorbed by the more infusible portion, binds the whole into a solid mass on cooling: such substances are found in felspar, and in a small admixture of calcic or alkaline silicate. The clay employed in porcelain-making is always directly derived from decomposed felspar, none of the clays of the secondary strata being pure enough for the purpose: it must be white, and free from iron oxide. To diminish the contraction which this substance undergoes in the fire, a quantity of finely divided silica, carefully prepared by crushing and grinding calcined flints or chert, is added, together with a proper proportion of felspar or other fusible material, also reduced to impalpable powder. The utmost pains are taken to effect perfect uniformity of mixture, and to avoid the introduction of particles of grit, or other foreign bodies. The ware itself is fashioned either on the potter's wheel — a kind of vertical lathe — or in moulds of plaster of Paris, and dried first in the air, afterwards by artificial heat, and at length completely hardened by exposure to the temperature of ignition. The porous *biscuit* is now fit to receive its glaze, which may be either ground felspar, or a mixture of gypsum, silica, and a little porcelain clay, diffused through water. The piece is dipped for a moment into this mixture, and withdrawn; the water sinks into its substance, and the powder remains evenly spread upon its surface; it is once more dried, and, lastly, fired at an exceedingly high temperature.

The porcelain-furnace is a circular structure of masonry, having several fireplaces, and surmounted by a lofty dome. Dry wood or coal is consumed as fuel, and its flame directed into the interior, and made to circulate around and among the earthen cases, or *seggars*, in which the articles to be fired are packed. Many hours are required for this operation, which must be very carefully managed. After the lapse of several days, when the furnace has completely cooled, the contents are removed in a finished state, so far as regards the ware.

The ornamental part, consisting of gilding and painting in enamel, has yet to be executed; after which the pieces are again heated, in order to flux the colors. The operation has sometimes to be repeated more than once.

* See Richardson and Watts's Chemical Technology, vol. i. part iv. pp. 69-104.

The manufacture of porcelain in Europe is of modern origin: the Chinese have possessed the art from the commencement of the seventh century, and their ware is, in some respects, altogether unequalled. The materials employed by them are known to be *kaolin*, or decomposed felspar; *petuntze*, or quartz reduced to fine powder; and the ashes of fern, which contain potassium carbonate.

Stoneware. — This is a coarse kind of porcelain, made from clay containing oxide of iron and a little lime, to which it owes its partial fusibility. The glazing is performed by throwing common salt into the heated furnace: this is volatilized, and decomposed by the joint agency of the silica of the ware and of the vapor of water always present; hydrochloric acid and soda are produced, the latter forming a silicate, which fuses over the surface of the ware, and gives a thin, but excellent glaze.

Earthenware. — The finest kind of earthenware is made from a white secondary clay, mixed with a considerable quantity of silica. The articles are thoroughly dried and fired; after which they are dipped into a readily fusible glaze mixture, of which lead oxide is usually an important ingredient, and, when dry, re-heated to the point of fusion of the latter. The whole process is much easier of execution than the making of porcelain, and demands less care. The ornamental designs in blue and other colors, so common upon plates and household articles, are printed upon paper in enamel pigment mixed with oil, and transferred, while still wet, to the unglazed ware. When the ink becomes dry, the paper is washed off, and the glazing completed.

The coarser kinds of earthenware are sometimes covered with a whitish opaque glaze, which contains the oxides of lead and tin; such glaze is very liable to be attacked by acids, and is dangerous for culinary vessels.

Crucibles, when of good quality, are very valuable to the practical chemist. They are made of clay free from lime, mixed with sand or ground ware of the same description. The Hessian and Cornish crucibles are among the best. Sometimes a mixture of plumbago and clay is employed for the same purpose; and powdered coke has been also used with the earth: such crucibles bear rapid changes of temperature with impunity.

GROUP III.

MAGNESIUM.

Atomic weight, 24. Symbol, Mg.

This metal was formerly classed with the metals of the alkaline earths, but it is much more nearly related to zinc by its properties in the free state, as well as by the volatility of its chloride, the solubility of its sulphate, and the isomorphism of several of its compounds with the analogously constituted compounds of zinc.

Magnesium occurs in the mineral kingdom as hydrate, carbonate, borate, phosphate, sulphate, and nitrate, sometimes in the solid state, sometimes dissolved in mineral waters: magnesian limestone, or dolomite, which forms entire mountain masses, is a carbonate of magnesium and calcium. Magnesium also occurs as silicate, combined with other silicates, in a variety of minerals, as steatite, hornblende, augite, talc, &c.; also as aluminate in spinelle and zeilanite. It likewise occurs in the bodies of plants and animals, chiefly as carbonate and phosphate, and in combination with organic acids.

Metallic magnesium is prepared:

1. By the electrolysis of fused magnesium chloride, or, better, of a mix-

ture of 4 molecules of magnesium chloride and 3 molecules of potassium chloride with a small quantity of sal-ammoniac. A convenient way of effecting the reduction is to fuse the mixture in a common clay tobacco-pipe over an Argand spirit-lamp or gas-burner, the negative pole being an iron wire passed up the pipe-stem, and the positive pole a piece of gas-coke, just touching the surface of the fused chlorides. On passing the current of a battery of ten Bunsen's cells through the arrangement, the magnesium collects round the extremity of the iron wire (Matthiessen).

2. Magnesium may be prepared in much larger quantity by reducing magnesium chloride, or the double chloride of magnesium and sodium or potassium, with metallic sodium. The double chloride is prepared by dissolving magnesium carbonate in hydrochloric acid, adding an equivalent quantity of sodium or potassium chloride, evaporating to dryness, and fusing the residue. This product, heated with sodium in a wrought-iron crucible, yields metallic magnesium, containing certain impurities, from which it may be freed by distillation. This process is now carried out on the manufacturing scale, and the magnesium is drawn out into wire or formed into riband for burning.*

Magnesium is a brilliant metal, almost as white as silver, somewhat more brittle at common temperatures, but malleable at a heat a little below redness. Its specific gravity is 1·74. It melts at a red heat, and volatilizes at nearly the same temperature as zinc. It retains its lustre in dry air, but in moist air it becomes covered with a crust of magnesia.

Magnesium in the form of wire or riband takes fire at a red heat, burning with a dazzling bluish-white light. The flame of a candle or spirit-lamp is sufficient to inflame it, but to insure continuous combustion the metal must be kept in contact with the flame. For this purpose lamps are constructed, provided with a mechanism which continually pushes three or more magnesium wires into a small spirit-flame.

The magnesium flame produces a continuous spectrum, containing a very large proportion of the more refrangible rays: hence it is well adapted for photography, and has, indeed, been used for taking photographs, in the absence of the sun, or in places where sunlight cannot penetrate, as in caves or subterranean apartments.

Magnesium Chloride, $MgCl_2$. — When magnesia, or its carbonate, is dissolved in hydrochloric acid, magnesium chloride and water are produced; but when this solution is evaporated to dryness, the last portions of water are retained with such obstinacy, that decomposition of the water is brought about by the concurring attractions of magnesium for oxygen, and of chlorine for hydrogen; hydrochloric acid is expelled, and magnesia remains. If, however, sal-ammoniac, potassium chloride, or sodium chloride is present, a double salt is produced, which is easily rendered anhydrous. The best mode of preparing the chloride is to divide a quantity of hydrochloric acid into two equal portions, to neutralize one with magnesia, and the other with ammonia, or carbonate of ammonia: to mix these solutions, evaporate them to dryness, and then expose the salt to a red heat in a loosely covered porcelain crucible. Sal-ammoniac sublimes, and magnesium chloride in a fused state remains; the latter is poured out upon a clean stone, and when cold transferred to a well stopped bottle.

The chloride so obtained is white and crystalline. It is very deliquescent and highly soluble in water, from which it cannot again be recovered by evaporation, for the reasons just mentioned. When long exposed to the air in a melted state, it is converted into magnesia. It is soluble in alcohol.

* For details of the manufacturing process, see Richardson and Watts's Chemical Technology, vol. i. pt. v. pp. 336–339.

Magnesium Oxide, or Magnesia, MgO. — This oxide is easily prepared by exposing the *magnesia alba* of pharmacy, which is a hydro-carbonate, to a full red heat in an earthen or platinum crucible. It forms a soft, white powder, which slowly attracts moisture and carbonic acid from the air, and unites quietly with water to a hydrate which possesses a feeble degree of solubility, requiring about 5000 parts of water at 15.5° and 36,000 parts at 100°. The alkalinity of magnesia can only be observed by placing a small portion in a moistened state upon test-paper; it neutralizes acids, however, in the most complete manner. It is infusible.

Magnesium sulphide is formed by passing vapor of carbon sulphide over magnesia, in capsules of coke, at a strong red heat.

Magnesium Sulphate; Epsom Salt; $SO_4Mg.7OH_2$. — This salt occurs in sea-water, and in that of many mineral springs, and is now manufactured in large quantities by acting on magnesian limestone with dilute sulphuric acid, and separating the magnesium sulphate from the greater part of the slightly soluble calcium sulphate by filtration. The crystals are derived from a right rhombic prism; they are soluble in an equal weight of water at 15·5°, and in a still smaller quantity at 100°. The salt has a nauseous bitter taste, and, like many other neutral salts, possesses purgative properties. When it is exposed to heat, 6 molecules of water readily pass off, the seventh being energetically retained. Magnesium sulphate forms beautiful double salts with the sulphates of potassium and ammonium, which contain 6 molecules of crystallization-water, their formulæ being $(SO_4)_2Mg''K_2.6OH_2$, and $(SO_4)_2Mg''(NH_4)_2.6OH_2$. These salts are isomorphous, and form monoclinic crystals.

Magnesium Carbonate. — The *neutral carbonate*, CO_3Mg or $CO_2.MgO$, occurs native in rhombohedral crystals, resembling those of calc-spar, imbedded in talc slate: a soft earthy variety is sometimes met with.

When magnesia alba is dissolved in aqueous carbonic acid, and the solution left to evaporate spontaneously, small prismatic crystals are deposited, consisting of trihydrated magnesium carbonate, $CO_3Mg.3OH_2$.

The magnesia alba itself, although often called carbonate of magnesium, is not so in reality; it is a compound of carbonate with hydrate. It is prepared by mixing hot solutions of potassium or sodium carbonate and magnesium sulphate, the latter being kept in slight excess, boiling the whole a few minutes, during which time much carbonic acid is disengaged, and well washing the precipitate so produced. If the solution be very dilute, the magnesia alba is exceedingly light and bulky; if otherwise, it is denser. The composition of this precipitate is not perfectly constant. In most cases it contains $4CO_3Mg.MgH_2O_2.6OH_2$.

Magnesia alba is slightly soluble in water, especially when cold.

Magnesium Phosphate, $PO_4Mg''H.7OH_2$. — This salt separates in small colorless prismatic crystals when solutions of sodium phosphate and magnesium sulphate are mixed and suffered to stand for some time. According to Graham, it is soluble in about 1000 parts of cold water. Magnesium phosphate exists in the grain of the cereals, and can be detected in considerable quantity in beer.

Magnesium and Ammonium Phosphate, $PO_4Mg''(NH_4).6OH_2$. — When ammonia or its carbonate is mixed with a magnesium salt, and a soluble phosphate is added, a crystalline precipitate having the above composition, subsides, immediately if the solutions are concentrated, and after some time if very dilute: in the latter case, the precipitation is promoted by stirring. This salt is slightly soluble in pure water, but nearly insoluble

in saline and ammoniacal liquids. When heated, it gives off water and ammonia, and is converted into *magnesium pyrophosphate*, $P_2O_7Mg_2$:

$$2PO_4Mg(NH_4) = P_2O_7Mg_2 + OH_2 + 2NH_3.$$

At a strong red-heat it fuses to a white enamel-like mass. Magnesium and ammonium phosphate sometimes form a urinary calculus, and occur also in guano.

In practical analysis, magnesium is often separated from solutions by bringing it into this state. The liquid, free from alumina, lime, &c., is mixed with sodium phosphate and excess of ammonia, and gently heated for a short time. The precipitate is collected upon a filter and thoroughly washed with water containing a little ammonia, after which it is dried, ignited to redness, and weighed. The proportion of magnesia is then easily calculated.

Magnesium Silicates. — The following natural compounds belong to this class: *Chrysolite*, $SiO_4Mg_2 = SiO_2.2MgO$, a crystallized mineral, sometimes employed for ornamental purposes: a portion of the magnesia is commonly replaced by ferrous oxide, which communicates a green color. *Meerschaum*. $2SiO_3Mg.SiO_2 = 3SiO_2.2MgO$, a soft, sectile mineral, from which pipe-bowls are made. *Talc*. $4SiO_3Mg.SiO_2 . \frac{4}{3}$ aq. (called *steatite* when massive), is a soft, white sectile, transparent or translucent mineral, used as fire-stones for furnaces and stoves, and in thin plates for glazing lanterns, &c.; also in the state of powder for diminishing friction. *Soapstone*, also called steatite, is a silicate of magnesium and aluminium of somewhat variable composition. *Serpentine* is a combination of silicate and hydrate of magnesium. *Jade*, an exceedingly hard stone, brought from New Zealand, is a silicate of magnesium and aluminium: its green color is due to chromium. *Augite* and *hornblende* are essentially double salts of silicic acid, magnesia, and lime, in which the magnesia is more or less replaced by its isomorphous substitute, ferrous oxide.

Magnesium salts are isomorphous with zinc salts, ferrous salts, cupric salts, cobalt salts, and nickel salts, &c.; they are usually colorless, and are easily recognized by the following characters: — A gelatinous white precipitate with *caustic alkalies*, including *ammonia*, insoluble in excess, but soluble in solution of sal-ammoniac. A white precipitate with *potassium* and *sodium carbonates*, but none with ammonium carbonate in the cold. A white crystalline precipitate with soluble *phosphates*, on the addition of a little ammonia.

ZINC.

Atomic weight, 65. Symbol, Zn.

Zinc is a somewhat abundant metal: it is found in the state of carbonate, silicate, and sulphide, associated with lead ores in many districts, both in Britain and on the Continent; large supplies are obtained from Silesia, and from the neighborhood of Aachen. The native carbonate, or *calamine*, is the most valuable of the zinc ores, and is preferred for the extraction of the metal: it is first roasted to expel water and carbonic acid, then mixed with fragments of coke or charcoal, and distilled at a full red heat in a large earthen retort; carbon monoxide escapes, while the reduced metal volatilizes and is condensed by suitable means, generally with minute quantities of arsenic.

Zinc is a bluish-white metal, which slowly tarnishes in the air; it has a lamellar, crystalline structure, a density varying from 6·8 to 7·2, and is, under ordinary circumstances, brittle. Between 120° and 150° C. (248°—300° F.) it is, on the contrary, malleable, and may be rolled or hammered without danger of fracture; and, what is very remarkable, after such treatment, it retains its malleability when cold; the sheet-zinc of commerce is thus made. At 210° C. (410° F.) it is so brittle that it may be reduced to powder. At 412° C. (773° F.) it melts: at a bright red heat it boils and volatilizes, and, if air be admitted, burns with a splendid greenish light, generating the oxide. Dilute acids dissolve zinc very readily: it is constantly employed in this manner for preparing hydrogen gas.

Zinc is a dyad metal, forming only one class of compounds.

Zinc Chloride, $ZnCl_2$, may be prepared by heating metallic zinc in chlorine: by distilling a mixture of zinc filings and corrosive sublimate; or, more easily, by dissolving zinc in hydrochloric acid. It is a nearly white, translucent, fusible substance, very soluble in water and alcohol, and very deliquescent. A strong solution of zinc chloride is sometimes used as a bath for obtaining a graduated heat above 100°. Zinc chloride unites with sal-ammoniac and potassium chloride to double salts: the former of these, made by dissolving zinc in hydrochloric acid, and then adding an equivalent quantity of sal-ammoniac, is very useful in tinning and soft-soldering copper and iron.

Zinc Oxide, ZnO, is a strong base, forming salts isomorphous with the magnesium salts. It is prepared either by burning zinc in atmospheric air, or by heating the carbonate to redness. Zinc oxide is a white, tasteless powder, insoluble in water, but freely dissolved by acids. When heated it is yellow, but turns white again on cooling. It is getting into use as a substitute for white lead. To prepare zinc-white on a large scale, metallic zinc is volatilized in large earthen muffles, whence the zinc vapor passes into a small receiver (*guérite*), where it comes in contact with a current of air and is oxidized. The zinc oxide thus formed passes immediately into a condensing chamber divided into several compartments by cloths suspended within it.

Zinc Sulphate, $SO_4Zn.7OH_2$, commonly called *white vitriol.*—This salt is hardly to be distinguished by the eye from magnesium sulphate: it is prepared either by dissolving the metal in dilute sulphuric acid, or, more economically, by roasting the native sulphide, or *blende*, which, by absorption of oxygen, becomes in great part converted into sulphate. The altered mineral is thrown hot into water, and the salt obtained by evaporating the clear solution. Zinc sulphate has an astringent metallic taste, and is used in medicine as an emetic. The crystals dissolve in $2\frac{1}{2}$ parts of cold, and in a much smaller quantity of hot water. Crystals containing 6 molecules of water have been observed. Zinc sulphate forms double salts with the sulphates of potassium and ammonium, namely, $(SO_4)_2ZnK_2.6OH_2$, and $(SO_4)_2Zn(NH_4)_2.6OH_2$, isomorphous with the corresponding magnesium salts.

Zinc Carbonate, CO_3Zn, is found native; the white precipitate obtained by mixing solutions of zinc and of alkaline carbonates, is a combination of carbonate and hydrate. When heated to redness, it yields pure zinc oxide.

Zinc Sulphide, ZnS, occurs native as *blende*, in regular tetrahedrons, dodecahedrons, and other monometric forms, and of various colors, from white or yellow to brown or black, according to its degree of purity: it is a valuable ore of zinc. A variety called *black jack* occurs somewhat abundantly in Derbyshire, Cumberland, and Cornwall. A *hydrated sulphide*, ZnS.

OH_2, is obtained as a white precipitate on adding an alkaline sulphide to the solution of a zinc salt.

Zinc salts are distinguished by the following characters: — *Caustic potash* and *soda* give a white precipitate of hydrate, freely soluble in excess of alkali. *Ammonia* behaves in the same manner; an excess redissolves the precipitate instantly. *Potassium* and *sodium carbonates* give white precipitates, insoluble in excess. *Ammonium carbonate* gives also a white precipitate, which is redissolved by an excess. *Potassium ferrocyanide* gives a white precipitate. *Hydrogen sulphide* causes no change in zinc solutions containing free mineral acids: but in neutral solutions, or with zinc salts of organic acids, such as the acetate, a white precipitate is formed. *Ammonium sulphide* throws down white sulphide of zinc, insoluble in caustic alkalies. The formation of this precipitate in a solution containing excess of caustic alkali, serves to distinguish zinc from all other metals.

All zinc compounds, heated on charcoal with sodium carbonate in the inner blowpipe flame, give an incrustation of zinc oxide, which is yellow while hot, but becomes white in cooling. If this incrustation be moistened with a dilute solution of cobalt nitrate, and strongly heated in the outer flame, a fine green color is produced.

The applications of metallic zinc to the purposes of roofing, the construction of water-channels, &c., are well known; it is sufficiently durable, but inferior in this respect to copper. It is much used also for protecting iron and copper from oxidation when immersed in saline solutions, such as sea-water, or exposed to damp air. This it does by forming an electric circuit, in which it acts as the positive or more oxidable metal (p. 249). *Galvanized iron* consists of iron having its surface coated with zinc.

CADMIUM.

Atomic weight, 112. Symbol, Cd.

This metal was discovered in 1817 by Stromeyer, and by Hermann: it accompanies the ores of zinc, especially those occurring in Silesia, and, being more volatile than that substance, rises first in vapor when the calamine is subjected to distillation with charcoal. Cadmium resembles tin in color, but is somewhat harder: it is very malleable, has a density of 8·7, melts below 260° C. (500° F.), and is nearly as volatile as mercury. It tarnishes but little in the air, but, when strongly heated, burns. Dilute sulphuric and hydrochloric acids act but little on this metal in the cold; nitric acid is its best solvent.

The observed vapor-density of cadmium is 3·94 compared with air as unity, or 56·3 compared with hydrogen, which latter number does not differ greatly from the half of 112, the atomic weight of the metal: hence it appears that the *atom* of cadmium in the state of vapor occupies twice the space of an atom of hydrogen (see p. 229).

Cadmium, like zinc, is dyadic, and forms but one series of compounds.

Cadmium Oxide, CdO. — This oxide may be prepared by igniting either the carbonate or the nitrate: in the former case it has a pale-brown color, and in the latter a much darker tint, and forms octohedral microscopic crystals. Cadmium oxide is infusible: it dissolves in acids, producing a

series of colorless salts: it attracts carbonic acid from the air, and turns white.

Cadmium Sulphate, $SO_4Cd.4OH_2$, is easily obtained by dissolving the oxide or carbonate in dilute sulphuric acid: it is very soluble in water, and forms double salts with the sulphates of potassium and ammonium, which contain respectively $(SO_4)_2CdK_2.6OH_2$ and $(SO_4)_2Cd(NH_4).6OH_2$.

Cadmium Chloride, $CdCl_2$, is a very soluble salt, crystallizing in small four-sided prisms.

Cadmium Sulphide is a very characteristic compound, of a bright-yellow color, forming microscopic crystals, fusible at a high temperature. It is obtained by passing sulphuretted hydrogen gas through a solution of the sulphate, nitrate, or chloride. This compound is used as a yellow coloring matter, of great beauty and permanence. It occurs native as *greenockite*.

The salts of cadmium are thus distinguished: — Fixed caustic *alkalies* give a white precipitate of hydrated oxide, insoluble in excess. *Ammonia* gives a similar white precipitate, readily soluble in excess. The *fixed alkaline carbonates*, and ammonia carbonate, throw down white cadmium carbonate, insoluble in excess of either precipitant. *Hydrogen sulphide* and *ammonium sulphide* precipitate the yellow sulphide of cadmium.

GROUP IV.

COPPER.

Atomic weight, 63·5. Symbol, Cu (Cuprum).

Copper is a metal of great value in the arts; it sometimes occurs in the metallic state, crystallized in octohedrons, or more frequently in dodecahedrons, but is more abundant in the form of red oxide, and in that of sulphide combined with sulphide of iron, as *yellow copper ore*, or *copper pyrites*. Large quantities of the latter substance are annually obtained from the Cornish mines, and taken to South Wales for reduction, which is effected by a somewhat complex process. The principle of this may, however, be easily made intelligible. The ore is roasted in a reverberatory furnace, by which much of the iron sulphide is converted into oxide, while the copper sulphide remains unaltered. The product of this operation is then strongly heated with siliceous sand; the latter combines with the iron oxide to a fusible *slag*, and separates from the heavier copper-compound. When the iron has, by a repetition of these processes, been got rid of, the copper sulphide begins to decompose in the flame-furnace, losing its sulphur and absorbing oxygen: the temperature is then raised sufficiently to reduce the oxide thus produced, by the aid of carbonaceous matter. The last part of the operation consists in thrusting into the melted metal a pole of birch-wood, the object of which is probably to reduce a little remaining oxide by the combustible gases thus generated. Large quantities of extremely valuable ore, chiefly carbonate and red oxide, have lately been obtained from South Australia and Chile.

Copper has a well-known yellowish-red color, a specific gravity of 8·96, and is very malleable and ductile: it is an excellent conductor of heat and electricity; it melts at a bright red heat, and seems to be slightly volatile at a very high temperature Copper undergoes no change in dry air; exposed to a moist atmosphere, it becomes covered with a strongly adherent

green crust, consisting in a great measure of carbonate. Heated to redness in the air, it is quickly oxidized, becoming covered with a black scale. Dilute sulphuric and hydrochloric acids scarcely act upon copper; boiling oil of vitriol attacks it, with evolution of sulphurous oxide; nitric acid, even dilute, dissolves it readily, with evolution of nitrogen dioxide.

Copper is a dyad metal, its most stable compounds, the *cupric* compounds, containing 1 atom of the metal combined with 2 atoms of a univalent, or 1 atom of a bivalent negative radical, *e.g.*, $Cu''Cl_2$, $Cu''O$, $Cu''(NO_3)_2$, $Cu''SO_4$, &c. Some of these, however, are capable of taking up another atom of copper, and forming compounds, called *cuprous* compounds, in which the copper is apparently univalent; thus cuprous chloride, $Cu_2Cl_2 = \left|\begin{matrix}Cu\\Cu\end{matrix}\right\rangle Cl_2$; cuprous oxide, $Cu_2O = \left|\begin{matrix}Cu\\Cu\end{matrix}\right\rangle O$. These compounds are very unstable, being easily converted into cupric compounds by the action of oxidizing agents.

Copper Chlorides. — *Cupric chloride*, $CuCl_2$, is most easily prepared by dissolving cupric oxide in hydrochloric acid, and concentrating the green solution thence resulting. It forms green crystals, $CuCl_2.2OH_2$, very soluble in water and in alcohol: it colors the flame of the latter green. When gently heated, it parts with its water of crystallization and becomes yellowish-brown; at a high temperature it loses half its chlorine and becomes converted into *cuprous chloride*. The latter is a white fusible substance, but little soluble in water, and prone to oxidation: it is formed when copper-filings or copper-leaf are put into chlorine gas; also by precipitating a solution of cupric chloride or other cupric salt with stannous chloride:

$2CuCl_2$	+	$SnCl_2$	=	Cu_2Cl_2	+	$SnCl_4$
Cupric chloride.		Stannous chloride.		Cuprous chloride.		Stannic chloride.

A plate of copper immersed in hydrochloric acid in a vessel containing air, becomes covered with white tetrahedrons of cuprous chloride. This compound dissolves in hydrochloric acid, forming a colorless solution, which gradually turns blue on exposure to the air.

A *hydrated cupric oxychloride*, $CuCl_2.3CuH_2O_2$, occurs native as *atacamite*.

Both the chlorides of copper form double salts with the chlorides of the alkali-metals.

Cuprous Hydride, Cu_2H_2. —When a solution of cupric sulphate is heated to about 70°, with hypophosphorous acid, this compound is deposited as a yellow precipitate which soon turns red-brown. It gives off hydrogen when heated, takes fire in chlorine gas, and is converted by hydrochloric acid into cuprous chloride, with evolution of a double quantity of hydrogen, the acid giving up its hydrogen as well as the copper hydride:

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

This reaction affords a remarkable instance of the union of two atoms of the same element to form a molecule (see page 232).

Copper Oxides. — Two oxides of copper are known, corresponding to the chlorides; and a very unstable dioxide or peroxide, CuO_2, is said to be formed, as a yellowish-brown powder, by the action of hydrogen dioxide on cupric hydrate.

Copper Monoxide, Cupric oxide, or *Black oxide of copper*, CuO, is prepared by calcining metallic copper at a red-heat, with full exposure to air, or more conveniently, by heating the nitrate to redness, which suffers com-

plete decomposition. Cupric salts mixed with caustic alkali in excess, yield a bulky pale-blue precipitate of hydrated cupric oxide, or cupric hydrate, CuH_2O_2 or $CuO.OH_2$, which, when the whole is raised to the boiling-point, becomes converted into a heavy dark-brown powder: this also is anhydrous oxide of copper, the hydrate suffering decomposition, even in contact with water. The oxide prepared at a high temperature is perfectly black and very dense. Cupric oxide is soluble in acids, and forms a series of very important salts, isomorphous with magnesium salts.

Cuprous oxide, Cu_2O, also called *Red oxide* and *Suboxide of copper*. — This oxide may be obtained by heating in a covered crucible a mixture of 5 parts of black oxide and 4 parts of fine copper-filings; or by adding grape-sugar to a solution of cupric sulphate, and then putting in an excess of caustic potash; the blue solution, heated to ebullition, is reduced by the sugar, and deposits cuprous oxide. This oxide often occurs in beautiful transparent ruby-red crystals, associated with other ores of copper, and can be obtained in the same state by artificial means. It communicates to glass a magnificent red tint, while that given by the cupric oxide is green.

Cuprous oxide dissolves in excess of hydrochloric acid, forming a solution of cuprous chloride, from which that compound is precipitated on dilution with water. Most oxygen-acids, namely, sulphuric, phosphoric, acetic, oxalic, tartaric, and citric acids, decompose cuprous oxide, forming cupric salts, and separating metallic copper; nitric acid converts it into cupric nitrate. Hence there are but few cuprous oxygen-salts, none indeed excepting the sulphites and certain double sulphites formed by mixing a cupric solution with the sulphite of an alkali-metal, *e.g.*, ammonio-cuprous sulphite, $SO_3Cu'(NH_4)$.

Cupric Sulphate, $SO_4Cu.5OH_2$. — This beautiful salt, commonly called *blue vitriol*, is prepared by dissolving cupric oxide in sulphuric acid, or, at less expense, by oxidizing the sulphide. It forms large blue crystals, soluble in four parts of cold and two parts of boiling water; when heated to 100° C. (212° F.) it readily loses four molecules of crystallization-water; but the fifth is retained with great pertinacity, and is expelled only at a low red heat. At a very high temperature, cupric sulphate is entirely converted into cupric oxide, with evolution of sulphurous oxide and oxygen. Cupric sulphate combines with the sulphates of potassium and of ammonium, forming pale-blue salts, $(SO_4)_2CuK_2.6OH_2$ and $(SO_4)_2Cu(NH_4)_2.6OH_2$, isomorphous with the corresponding magnesium salts.

Cupric Nitrate, $(NO_3)_2Cu.3OH_2$, is easily made by dissolving the metal in nitric acid; it forms deep-blue crystals, very soluble and deliquescent. It is highly corrosive. An insoluble basic nitrate is known; it is green.

Cupric Carbonates. — When sodium carbonate is added in excess to a solution of cupric sulphate, the precipitate is at first pale-blue and flocculent, but by warming it becomes sandy, and assumes a green tint; in this state it contains $CO_3Cu.CuH_2O_2$+aq. This substance is prepared as a pigment. The beautiful mineral *malachite* has a similar composition, but contains no water of crystallization, its composition being $CO_3Cu.CuH_2O_2$. Another natural compound, called *azurite*, not yet artificially imitated, occurs in large transparent crystals of the most intense blue: it contains $2CO_3Cu.CuH_2O_2$. *Verditer*, made by decomposing cupric nitrate with chalk, is said, however, to have a somewhat similar composition.

Cupric Arsenite is a bright-green insoluble powder, prepared by mixing the solutions of a cupric salt with an alkaline arsenite.

Copper Sulphides.—There are two well-defined copper sulphides, anal-

ogous in composition to the oxides, and four others, containing larger proportions of sulphur, but of less defined constitution; these latter are precipitated from solutions of cupric salts by potassium pentasulphide.

Cupric Sulphide, CuS, occurs native as *indigo copper* or *covellin*, in soft bluish-black hexagonal plates and spheroïdal masses, and is produced artificially by precipitating cupric salts with hydrogen sulphide.

Cuprous Sulphide, Cu_2S, occurs native as *copper-glance* or *redruthite*, in lead-gray hexagonal prisms, belonging to the rhombic system; it is produced artificially by the combustion of copper-foil in sulphur vapor, by igniting cupric oxide with sulphur, and by other methods. It is a powerful sulphur-base, uniting with the sulphides of antimony, arsenic, and bismuth, to form several natural minerals. The several varieties of fahl-ore, or tetrahedrite, consist of cuprous sulphantimonite or sulpharsenite, in which the copper is more or less replaced by equivalent quantities of iron, zinc, silver, and mercury. The important ore, called *copper-pyrites*, is a cuproso-ferric sulphide, $Cu'Fe'''S_2$, or $Cu_2S.Fe_2S_3$, occurring in tetrahedral crystals of the quadratic system, or in irregular masses. Another species of copper and iron sulphide, containing various proportions of the two metals, occurs native, as *purple copper* or *erubescite*, in cubes, octohedrons, and other monometric forms.

Ammoniacal Copper Compounds. — The chlorides, sulphate, nitrate, and other salts of copper, unite with one or more molecules of ammonia, forming, for the most part, crystalline compounds of blue or green color, some of which may be regarded as salts of metallammoniums (p. 315). Thus, cupric chloride forms with ammonia, the compounds, $2NH_3.CuCl_2$, $4NH_3.CuCl_2$, and $6NH_3.CuCl_2$, the first of which may be formulated as *cupro-diammonium chloride*, $(N_2H_6Cu'')Cl_2$. Cupric sulphate forms, in like manner, *cupro-diammonium sulphate*, $(N_2H_6Cu'')SO_4$, which is a deep-blue crystalline salt. Cuprous iodide forms with ammonia the compound, $4NH_3.Cu_2I_2$.

The characters of the cupric salts are well marked.

Caustic *potash* gives a pale-blue precipitate of cupric hydrate, becoming blackish-brown anhydrous oxide on boiling. — *Ammonia* also throws down the hydrate; but, when in excess, redissolves it, yielding an intense purplish-blue solution. — *Potassium* and *sodium carbonates* give pale-blue precipitates of cupric carbonate, insoluble in excess. — *Ammonium carbonate*, the same, but soluble with deep-blue color. — *Potassium ferrocyanide* gives a fine red-brown precipitate of cupric ferrocyanide. — *Hydrogen sulphide* and *ammonium sulphide* afford black cupric sulphide, insoluble in ammonium sulphide.

The alloys of copper are of great importance. *Brass* consists of copper alloyed with from 28 to 34 per cent. of zinc; the latter may be added directly to the melted copper, or granulated copper may be heated with calamine and charcoal-powder, as in the old process. *Gun-metal*, a most valuable alloy, consists of 90 parts copper and 10 tin. *Bell* and *speculum metal* contain a still larger proportion of tin; these are brittle, especially the last named. A good bronze for statues is made of 91 parts copper, 2 parts tin, 6 parts zinc, and 1 part lead. The *brass* or *bronze* of the ancients is an alloy of copper with tin, often also containing lead, and sometimes zinc.

MERCURY.

Atomic weight, 200. Symbol, Hg. (Hydrargyrum).

This very remarkable metal, sometimes called *quicksilver*, has been known from early times, and perhaps more than all others has excited the attention and curiosity of experimenters, by reason of its peculiar physical properties. Mercury is of great importance in several of the arts, and enters into the composition of many valuable medicaments.

Metallic mercury is occasionally met with in globules disseminated through the native sulphide, which is the ordinary ore. This latter substance, sometimes called *cinnabar*, is found in considerable quantity in several localities, of which the most celebrated are Almaden in Spain, and Idria in Austria. Only recently it has been discovered in great abundance, and of remarkable purity, in California and Australia. The metal is obtained by heating the sulphide in an iron retort with lime or scraps of iron, or by roasting it in a furnace, and conducting the vapors into a large chamber, where the mercury is condensed, while the sulphurous acid is allowed to escape. Mercury is imported into this country in bottles of hammered iron, containing seventy-five pounds each, and in a state of considerable purity. When purchased in smaller quantities, it is sometimes found adulterated with tin and lead, which metals it dissolves to some extent without much loss of fluidity. Such admixture may be known by the foul surface the mercury exhibits when shaken in a bottle containing air, and by the globules, when made to roll upon the table, leaving a train or tail.

Mercury has a nearly silver-white color, and a very high degree of lustre: it is liquid at all ordinary temperatures, and solidifies only when cooled to —40°. In this state it is soft and malleable. At 350° C. (662° F.) it boils, and yields a transparent, colorless vapor, of great density. The metal volatilizes, however, to a sensible extent at all temperatures above 19° or 21° C. (66° or 68° F.); below this point its volatility is imperceptible. The volatility of mercury at the boiling heat is singularly retarded by the presence of minute quantities of lead or zinc. The specific gravity of mercury at 15·5° is 13·59; that of frozen mercury about 14, great contraction taking place in the act of solidification.

Pure mercury is quite unalterable in the air at common temperatures, but when heated to near its boiling-point, it slowly absorbs oxygen, and becomes converted into a crystalline dark-red powder, which is the highest oxide. At a dull red heat this oxide is again decomposed into its constituents. Hydrochloric acid has little or no action on mercury, and the same may be said of sulphuric acid in a diluted state: when the latter is concentrated and boiling-hot, it oxidizes the metal, converting it into mercuric sulphate, with evolution of sulphurous oxide. Nitric acid, even dilute and in the cold, dissolves mercury freely, with evolution of nitrogen dioxide.

The observed vapor-density of mercury referred to air as unity is 6·7;* this referred to hydrogen is nearly 100;† that is to say, half the atomic weight of the metal: consequently the atom of mercury, like that of cadmium, occupies in the gaseous state twice the volume of an atom of hydrogen (see page 229).

Mercury forms two series of compounds; namely, the *mercuric compounds*, in which it is bivalent, as $Hg''Cl_2$, $Hg''O$, $Hg''SO_4$, &c., and the *mercurous*

* Bineau, Comptes Rendus, xlix. 799.

† $\frac{6·7}{0·6926} = 98·3.$

compounds, in which it is apparently univalent, as Hg_2Cl_2, Hg_2O, &c. These compounds are analogous in constitution to the cupric and cuprous compounds; and the mercurous compounds, like the latter, are easily converted into mercuric compounds by the action of oxidizing agents, which remove one atom of mercury; but they are, on the whole, much more stable than the cuprous compounds.

Mercury Chlorides. — *Mercuric Chloride*, $Hg''Cl_2$, commonly called *corrosive sublimate*. — This compound may be obtained by several different processes: (1) When metallic mercury is heated in chlorine gas, it takes fire and burns, producing this substance. (2) It may be made by dissolving mercuric oxide in hot hydrochloric acid, crystals of corrosive sublimate then separating on cooling. (3) Or, more economically, by subliming a mixture of equal parts of mercuric sulphate and dry common salt; and this is the plan generally followed. The decomposition is represented by the equation:

SO_4Hg	+	$2NaCl$	=	$HgCl_2$	+	SO_4Na_2.
Mercuric sulphate.		Sodium chloride.		Mercuric chloride.		Sodium sulphate.

Sublimed mercuric chloride forms a white transparent crystalline mass of specific gravity 5·43; it melts at 265° C. (509° F.); boils at 295° C. (563° F.), and volatilizes somewhat more easily than calomel, even at ordinary temperatures. Its observed vapor-density, referred to hydrogen as unity, is 140: and the density calculated from the formula $HgCl_2$, supposing that the molecule occupies the same space as a molecule or two atoms of hydrogen (p. 229) is $\frac{200 + 2 \times 35{\cdot}5}{2} = 135{\cdot}5$; the near agreement of this number with the observed result shows that the vapor is in the normal state of condensation.

Mercuric chloride dissolves in 16 parts of cold and 3 parts of boiling water, and crystallizes from a hot solution in long white prisms. Alcohol and ether also dissolve it with facility; the latter even withdraws it from a watery solution.

Mercuric chloride combines with a great number of other metallic chlorides, forming a series of beautiful double salts, of which the ancient *sal alembroth* may be taken as a good example: it contains $HgCl_2 . 2NH_4Cl . OH_2$. Corrosive sublimate absorbs ammoniacal gas with great avidity, generating the compound $HgCl_2 . NH_3$.

Mercuric chloride forms several compounds with mercuric oxide. These are produced by several processes, as when an alkaline carbonate is added in varying proportions to a solution of mercuric chloride. They differ greatly in color and physical character, and are mostly decomposed by water.

Mercuric chloride forms insoluble compounds with many of the azotized organic principles, as albumin, &c. It is perhaps to this property that its strong antiseptic properties are due. Animal and vegetable substances are preserved by it from decay, as in Kyan's method of preserving timber and cordage. Albumin is on this account an excellent antidote to corrosive sublimate in cases of poisoning.

Mercurous Chloride, Hg_2Cl_2, commonly called *Calomel*. — This very important substance may be easily and well prepared by pouring a solution of mercurous nitrate into a large excess of dilute solution of common salt. It falls as a dense white precipitate, quite insoluble in water; it must be thoroughly washed with boiling distilled water, and dried. Calomel is, however, generally procured by another and more complex process. Dry

mercuric sulphate is rubbed in a mortar with as much metallic mercury as it already contains, and a quantity of common salt, until the globules disappear, and a uniform mixture has been produced. This is subjected to sublimation, the vapor of the calomel being carried into an atmosphere of steam, or into a chamber containing air; it is thus condensed into a minutely divided state, and the laborious process of pulverization of the sublimed mass is avoided. The reaction is thus explained:

SO_4Hg	+	Hg	+	$2NaCl$	=	Hg_2Cl_2	+	SO_4Na_2
Mercuric sulphate.				Sodium chloride.		Mercurous chloride.		Sodium sulphate.

Pure calomel is a heavy, white, insoluble, tasteless powder: it rises in vapor at a temperature below redness, and is obtained by ordinary sublimation as a yellowish-white crystalline mass. It is as insoluble in cold diluted nitric acid as silver chloride; boiling-hot strong nitric acid oxidizes and dissolves it. Calomel is instantly decomposed by an alkali, or by lime-water, with production of mercurous oxide. It is sometimes apt to contain a little mercuric chloride, which would be a very dangerous contamination in calomel employed for medical purposes. This is easily discovered by boiling with water, filtering the liquid, and adding caustic potash. Any corrosive sublimate is indicated by a yellow precipitate.

The observed vapor-density of calomel, referred to hydrogen as unity, is 119·2. Now the formula Hg_2Cl_2, if it represents a molecule occupying in the gaseous state two volumes (*i. e.*, twice the volume of an atom of hydrogen, p. 229), would give a density nearly double of this: for $\frac{400 + 2 \times 35{\cdot}5}{2} = 235{\cdot}5$. Hence it might be inferred that the composition of calomel should rather be represented by the simpler formula HgCl, which would give for the vapor-density the number 117·75. But this formula (the adoption of which would, of course, involve that of similar formulæ for the other mercurous salts, *e. g.*, NO_3Hg for the nitrate) is objectionable on account of its inconsistency with the law of even numbers, according to which a dyad element like mercury can never unite with an uneven number of monad atoms (p. 232). Moreover, the frequent decomposition of mercurous salts into mercuric salts and free mercury is in favor of the supposition that their molecules contain two atoms of mercury; and the anomaly in the vapor-volume of calomel may be explained by supposing that the vapor of this compound, like that of many others, undergoes at high temperatures the change known as *dissociation* (p. 531), the two volumes of mercurous chloride, Hg_2Cl, being resolved into two volumes of mercuric chloride, $HgCl_2$, and two volumes of mercury, Hg. This supposition is, to some extent, warranted by the observation that calomel vapor amalgamates gold-leaf, and that corrosive sublimate may be detected in resublimed calomel.

Iodides. — *Mercuric Iodide*, $Hg''I_2$, is formed, when solution of potassium iodide is mixed with mercuric chloride, as a precipitate which is at first yellow, but in a few moments changes to a most brilliant scarlet, this color being retained on drying. This is the neutral iodide: it may be made, although of rather duller tint, by triturating equivalent quantities of iodine and mercury with a little alcohol. In preparing it by precipitation, it is better to weigh out the proper proportions of the two salts, as the iodide is soluble in an excess of either, more especially in excess of potassium iodide. Mercuric iodide exhibits a very remarkable case of dimorphism, attended with difference of color, which is red or yellow, according to the figure assumed. Thus, when the iodide is suddenly exposed to a high temperature, it becomes bright-yellow throughout, and yields a copious sublimate

of minute but brilliant yellow crystals. If in this state it be touched by a hard body, it instantly becomes red, and the same change happens spontaneously after a certain lapse of time. On the other hand, by a very slow and careful heating, a sublimate of red crystals, having a totally different form, may be obtained, which are permanent. The same kind of change happens with the freshly precipitated iodide, as Mr. Warington has shown, the yellow crystals first formed breaking up in the course of a few seconds from the passage of the salt to the red modification.*

Mercuric iodide forms double salts with the more basic or positive metallic iodides, as those of the alkali-metals and alkaline earth-metals; thus it dissolves in aqueous potassium iodide, and the hot solution deposits on cooling, crystals of potassio-mercuric iodide, $2(KI.HgI_2).3OH_2$.

Mercurous Iodide, Hg_2I_2, is formed when a solution of potassium iodide is added to mercurous nitrate: it then separates as a dirty yellow, insoluble precipitate, with a tinge of green. It may also be prepared by rubbing mercury and iodine together in a mortar in the proportion of 1 atom of the former to 1 atom of the latter, the mixture being moistened from time to time with a little alcohol.

Oxides. — *Monoxide*, or *Mercurous Oxide*, HgO, commonly called *Red Oxide of Mercury*, or *Red Precipitate*. — There are numerous methods by which this compound may be obtained. The following may be cited as the most important: (1) By exposing mercury in a glass flask with a long narrow neck, for several weeks, to a temperature approaching 315° C. (599° F.). The product has a dark red color, and is highly crystalline; it is the *red precipitate* of the old writers. (2) By cautiously heating any of the mercuric or mercurous nitrates to complete decomposition, whereby the acid is decomposed and expelled, oxidizing the metal to a maximum, if it happen to be in the state of mercurous salt. The product thus obtained is also crystalline and very dense, but has a much paler color than the preceding; while hot, it is nearly black. It is by this method that the oxide is generally prepared: it is apt to contain undecomposed nitrate, which may be discovered by strongly heating a portion in a test-tube: if red fumes are produced, or the odor of nitrous acid exhaled, the oxide has been insufficiently heated in the process of manufacture. (3) By adding caustic potash in excess to a solution of corrosive sublimate, by which a bright yellow precipitate of mercuric oxide is thrown down, which differs from the foregoing preparations merely in being destitute of crystalline texture and much more minutely divided. It must be well washed and dried.

Mercuric oxide is slightly soluble in water, communicating to the latter an alkaline reaction and metallic taste: it is highly poisonous. When strongly heated, it is decomposed, as before observed, into metallic mercury and oxygen gas.

Mercurous Oxide, Hg_2O; *Suboxide*, or *Gray Oxide of Mercury*. — This oxide is easily prepared by adding caustic potash to mercurous nitrate, or by digesting calomel in solution of caustic alkali. It is a dark gray, nearly black, heavy powder, insoluble in water, slowly decomposed by the action of light into metallic mercury and red oxide. The preparations known in pharmacy by the names *blue pill*, *gray ointment*, *mercury with chalk*, &c., often supposed to owe their efficacy to this substance, merely contain the finely divided metal.

Mercury Nitrates. — Nitric acid varies in its action upon mercury, according to the temperature. When cold and somewhat diluted, it forms only mercurous salts, and these are neutral or basic — *i. e.*, oxynitrates

* Memoirs of the Chemical Society of London, i. 85.

(p. 283) — as the acid or the metal happens to be in excess. When, on the contrary, the nitric acid is concentrated and hot, the mercury is raised to its highest state of oxidation, and a mercuric salt is produced. Both classes of salts are apt to be decomposed by a large quantity of water, giving rise to insoluble, or sparingly soluble basic compounds.

Mercuric Nitrates. — By dissolving mercuric oxide in excess of nitric acid, and evaporating gently, a syrupy liquid is obtained, which, enclosed in a bell-jar over lime or sulphuric acid, deposits bulky crystals and crystalline crusts, both having the composition $2(NO_3)_2Hg''.OH_2$. The same substance is deposited from the syrupy liquid as a crystalline powder by dropping it into concentrated nitric acid. The syrupy liquid itself appears to be a definite compound containing $(NO_3)_2Hg''.OH_2$. By saturating hot dilute nitric acid with mercuric oxide, a salt is obtained on cooling, which crystallizes in needles, permanent in the air, containing $(NO_3)_2Hg''.Hg''O.OH_2$. The preceding crystallized salts are decomposed by water, with production of compounds more and more basic as the washing is prolonged or the temperature of the water raised.

Mercurous Nitrate, $(NO_3)_2Hg_2.2OH_2$, forms large colorless crystals soluble in a small quantity of water without decomposition; it is made by dissolving mercury in an excess of cold dilute nitric acid.

When excess of mercury has been employed, a finely crystallized basic salt is deposited after some time, containing $2(NO_3)_2Hg_2.Hg_2O.3OH_2$, or $2N_2O_5.3Hg_2O.3OH_2$; this is also decomposed by water. The two salts are easily distinguished when rubbed in a mortar with a little sodium chloride; the neutral compound gives sodium nitrate and calomel; the basic salt, sodium nitrate and a black compound of calomel with mercurous oxide. A black substance, called *Hahnemann's soluble mercury*, is produced when ammonia in small quantity is dropped into a solution of mercurous nitrate: it contains $N_2O_5.3Hg_2O.2NH_3$, or, according to Kane, $N_2O_5.2Hg_2O.2NH_3$; the composition of this preparation evidently varies according to the temperature and the concentration of the solutions.

Mercury Sulphates. — *Mercuric Sulphate,* SO_4Hg'', is readily prepared by boiling together oil of vitriol and metallic mercury until the latter is wholly converted into a heavy white crystalline powder, which is the salt in question; the excess of acid is then removed by evaporation carried to perfect dryness. Equal weights of acid and metal may be conveniently employed. Water decomposes the sulphate, dissolving out an acid salt, and leaving an insoluble, yellow, basic compound, formerly called *turpith* or *turbeth mineral*, containing, according to Kane's analysis, $SO_4Hg''.2Hg''O$, or $SO_3.3Hg''O$. Long-continued washing with hot water entirely removes the remaining acid, and leaves pure mercuric oxide.

Mercurous Sulphate, SO_4Hg_2, falls as a white crystalline powder when sulphuric acid is added to a solution of mercurous nitrate: it is but slightly soluble in water.

Mercury Sulphides. — *Mercuric Sulphide,* HgS, occurs native as cinnabar, a dull red mineral, which is the most important ore of mercury. Hydrogen sulphide passed in small quantity into a solution of mercuric nitrate, or chloride, forms a white precipitate, which is a compound of mercuric sulphide with the salt itself. An excess of the gas converts the whole into sulphide, the color at the same time changing to black. When this black sulphide is sublimed, it becomes dark-red and crystalline, but undergoes no change of composition: it is then *cinnabar* or *vermilion.* Mercuric sulphide is most easily prepared by subliming an intimate mixture of 6 parts of mercury and 1 part of sulphur, and reducing the resulting cinnabar to very fine powder, the beauty of the tint depending much upon the extent

to which division is carried. The red or crystalline sulphide may also be formed directly, without sublimation, by heating the black precipitated substance in a solution of potassium pentasulphide; the mercuric sulphide is, in fact, soluble, to a certain extent, in the alkaline sulphides, and forms with them crystallizable compounds.

When vermilion is heated in the air, it yields metallic mercury and sulphurous oxide: it resists the action both of caustic alkali in solution, and of strong mineral acids, even nitric, and is attacked only by nitromuriatic acid.

Mercurous sulphide, Hg_2S, is obtained by passing hydrogen sulphide into a solution of mercurous nitrate, as a black precipitate, which is resolved at a gentle heat into mercuric sulphide and metallic mercury.

Ammoniacal Mercury Compounds. Mercurammonium Salts. — By the action of ammonia and its salts on mercury compounds, a variety of substances are formed which may be regarded as salts of mercurammoniums — that is, of ammonium-molecules in which the hydrogen is more or less replaced by mercury, in the proportion of 100 or 200 parts of mercury to 1 part of hydrogen, according as the compound is formed from a mercurous or a mercuric salt. The following are the most important of these compounds: —

Mercuric Compounds. — Mercuro-diammonium chloride, $(N_2H_6Hg'')Cl_2$, known in pharmacy as *fusible white precipitate*, is produced by adding potash to a solution of ammonio-mercuric chloride, $(2NH_4Cl.HgCl_2)$, or by dropping a solution of mercuric chloride into a boiling solution of sal-ammoniac containing free ammonia, as long as the resulting precipitate redissolves: it then separates on cooling in regular dodecahedrons. At a gentle heat it gives off ammonia, leaving a chloride of dimercur-ammonium and hydrogen, $(NH_2Hg'')Cl.HCl$:

$$N_2H_6Hg''Cl_2 = NH_3Hg''Cl_2 + NH_3.$$

Mercurammonium chloride, $(NH_2Hg'')Cl$. — This salt, known in pharmacy as *infusible white precipitate*, is formed by adding ammonia to a solution of mercuric chloride. When first produced, it is bulky and white, but by contact with hot water, or by much washing with cold water, it is converted into hydrated dimercurammonium chloride, $NHg''_2Cl.OH_2$.

Trimercuro-diammonium nitrate, $(N_2H_2Hg''_3)(NO_3)_2.2OH_2$, is formed as a white precipitate, on mixing a dilute and very acid solution of mercuric nitrate with very dilute ammonia.

Trimercuro-diamine, $N_2Hg''_3$, a compound derived from a double molecule of ammonia, N_2H_6, by substitution of 3 atoms of bivalent mercury for 6 atoms of hydrogen, is formed by passing dry ammonia gas over dry precipitated mercuric oxide:

$$3Hg''O + 2NH_3 = N_2Hg''_3 + 3OH_2.$$

The excess of oxide being removed by nitric acid, the trimercuro-diamine is obtained as a dark-brown powder, which explodes by heat, friction, percussion, or contact with oil of vitriol, almost as violently as nitrogen chloride.

Dimercurammonium chloride, $NHg''_2Cl.OH_2$, is obtained, as already observed, by boiling mercurodiammonium chloride (infusible white precipitate) with water. It is a heavy, granular, yellow powder, which turns white again when treated with sal-ammoniac.

Dimercurammonium iodide, $NHg''_2I.OH_2$. — This compound may be formed by digesting the corresponding chloride in a solution of potassium iodide; or by heating mercuric iodide with excess of aqueous ammonia:

$$2HgI_2 + 4NH_3 + OH_2 = NHg''_2I.OH_2 + 3NH_4I;$$

also by passing ammonia gas over mercuric oxy-iodide:

$$Hg''_4I_2O_3 + 2NH_3 = 2(NHg''_2I.OH_2) + OH_2;$$

and, lastly, by adding ammonia to a solution of potassio-mercuric iodide mixed with caustic potash:

$$2(2KI.HgI_2) + NH_3 + 3KHO = NHg''_2I.OH_2 + 7KI + 2OH_2.$$

This last reaction affords an extremely delicate test for ammonia. A solution of potassio-mercuric iodide is prepared by adding potassium iodide to a solution of corrosive sublimate, till a portion only of the resulting red precipitate is redissolved, then filtering, and mixing the filtrate with caustic potash. The liquid thus obtained forms, with a very small quantity of ammonia, either free or in the form of an ammoniacal salt, a brown precipitate soluble in excess of potassium iodide. This is called Nessler's test for ammonia.*

Dimercurammonium hydrate, NHg''_2HO. — This compound is formed by treating precipitated mercuric oxide with aqueous ammonia, or by treating either of the dimercurammonium salts with a caustic alkali. It is a brown powder, which dissolves in acids, yielding salts of dimercurammonium.

Dimercurammonium sulphate, $(NHg''_2)_2SO_4.2OH_2$, formerly called *ammoniacal turpethum*, is prepared by dissolving mercuric sulphate in ammonia, and precipitating the solution with water. It is a heavy white powder, yellowish when dry, resolved by heat into water, nitrogen, ammonia, and mercurous sulphate.

Mercurous Compounds. — *Mercurosammonium chloride*, $NH_2Hg'Cl$, is the black precipitate formed when dry calomel is exposed to the action of ammonia gas. When exposed to the air, it gives off ammonia and leaves white mercurous chloride. — *Dimercurosammonium chloride*, $NH_2Hg'_2Cl$, is formed, together with sal-ammoniac, by digesting calomel in aqueous ammonia:

$$Hg_2Cl_2 + 2NH_3 = NH_2Hg_2Cl + NH_4Cl.$$

It is gray when dry, and is not altered by boiling water. — *Dimercurosammonium nitrate*, $2(NH_2Hg_2)NO_3.OH_2$. This, according to Kane, is the composition of the velvet-black precipitate known as Hahnemann's soluble mercury, which is produced on adding ammonia to a solution of mercurous nitrate. According to C. G. Mitscherlich, on the other hand, the precipitate thus formed has the composition $2NH_3.N_2O_5.3Hg_2O$, which is that of a hydrated *trimercurosammonium nitrate*, $2(NHHg_3)NO_3.2OH_2$.

Reactions of Mercury Salts. — All mercury compounds are volatilized or decomposed by a temperature of ignition: those which fail to yield the metal by simple heating may in all cases be made to do so by heating in a test-tube with a little dry sodium carbonate. The metal is precipitated from its soluble combinations by a plate of copper, and also by a solution of *stannous chloride* used in excess.

Hydrogen sulphide, and *ammonium sulphide*, produce in solutions, both of mercuric and of mercurous salts, black precipitates insoluble in ammonium sulphide. In mercuric salts, however, if the quantity of the reagent added is not sufficient for complete decomposition, a white precipitate is formed, consisting of a compound of mercuric sulphide with the original salt, and often colored yellow or brown by excess of mercuric sulphide. An excess

* Chemical Gazette, 1856, pp. 445, 463.

of hydrogen sulphide, or ammonium sulphide, instantly turns the precipitate black. This reaction is quite characteristic of mercuric salts.

Mercuric salts are further distinguished by forming a yellow precipitate with caustic *potash* or *soda;* white with *ammonia* or *ammonium carbonate*, insoluble in excess: red-brown with *potassium* or *sodium carbonate*. With *potassium iodide* they yield a bright scarlet precipitate, soluble in excess, either of the mercuric salt or of the alkaline iodide.

Mercurous salts are especially characterized by forming with *hydrochloric acid* or *soluble chlorides*, a white precipitate which is turned black by ammonia. They also yield black precipitates with *caustic alkalies*, white with *alkaline carbonates*, soon turning black; greenish-yellow with *potassium iodide*.

Alloys of mercury with other metals are termed *amalgams:* mercury dissolves in this manner many of the metals, as gold, silver, tin, lead, &c. These combinations sometimes take place with considerable violence, as in the case of potassium, in which light and heat are produced; besides this, many of the amalgams crystallize after a while, becoming solid. The amalgam of tin used in silvering looking-glasses, and that of silver and of copper, sometimes employed for stopping hollow teeth, are examples.

CLASS III.—TRIAD METALS.

THALLIUM.

Atomic weight, 204. Symbol, Tl.

THIS element was discovered by Crookes, in 1861, in the seleniferous deposit of a lead-chamber of a sulphuric acid factory in the Hartz mountains, where iron pyrites is used for the manufacture of sulphuric acid. The name is derived from θαλλός, "green," because its existence was first recognized by an intense green line, appearing in the spectrum of a flame in which thallium is volatilized. It was at first suspected to be a metalloïd, but further examination proved it to be a true metal. It was first obtained in a distinct metallic form by Crookes towards the end of the year 1861, and soon afterwards by Lamy, who prepared it from the deposit in the lead-chamber of M. Kuhlmann, of Lille, where Belgian pyrites is employed for the manufacture of sulphuric acid.

Thallium appears to be very widely diffused as a constituent of iron and copper pyrites, though it never constitutes more than the 4000th part of the bulk of the ores. It has also been found in lepidolite from Moravia, in mica from Zinnwald in Bohemia, and in the mother-liquors of the salt works at Nauheim.

Thallium is most economically prepared from the flue-dust of pyrites burners. This substance is stirred up in wooden tubs with boiling water, and the clear liquor siphoned off from the deposit is mixed with excess of strong hydrochloric acid, which precipitates impure thallium monochloride. To obtain a pure salt, this crude chloride is added by small portions at a time to half its weight of hot oil of vitriol in a porcelain or platinum dish, the mixture being constantly stirred, and the heat continued till the whole of the hydrochloric acid and the greater portion of the excess of sulphuric acid are driven off. The fused acid sulphate is now to be dissolved in an excess of water, and an abundant stream of hydrogen sulphide passed through the solution. The precipitate, which may contain arsenic, antimony, bismuth, lead, mercury, and silver, is separated by filtration, and the filtrate is boiled till all free hydrogen sulphide is removed. The liquid is now to be rendered alkaline with ammonia, and boiled; the precipitate of iron oxide and alumina, which generally appears in this place, is filtered off: and the clear solution evaporated to a small bulk. Thallium sulphate then separates on cooling, in long, clear prismatic crystals.

Metallic thallium may be reduced from the solution of the sulphate, either by electrolysis, or by the action of zinc.

Thallium is a heavy metal, resembling lead in its physical properties. When freshly cut, it exhibits a brilliant metallic lustre and grayish color, somewhat between those of silver and lead, assuming a slight yellowish tint by friction with harder bodies. It is very soft, being readily cut with a knife, and making a streak on paper like plumbago. It is very malleable, is not easily drawn into wire, but may be readily squeezed into that form

by the process technically called "squirting." It has a highly crystalline structure, and crackles like tin when bent. It melts at 294°.

In contact with the air, thallium tarnishes more rapidly than lead, becoming coated with a thin layer of oxide, which preserves the rest of the metal.

The most characteristic property of thallium is the intense green color which the metal or any of its compounds impart to a colorless flame; and this color, when viewed by the spectroscope, is seen to be absolutely monochromatic, appearing as one intensely brilliant and sharp green line.

Thallium dissolves in hydrochloric, sulphuric, and nitric acids, the latter attacking it very energetically, with copious evolution of red vapors.

Thallium forms two classes of compounds — namely, the *thallious compounds*, in which it is univalent; and the *thallic compounds*, in which it is trivalent. Thus it forms two oxides, Tl_2O and Tl_2O_3, with corresponding chlorides, bromides, iodides, and oxygen-salts. In some of its chemical relations it resembles the alkali-metals, forming a readily soluble and highly alkaline monoxide, a soluble and alkaline carbonate, an insoluble platinochloride, a thallio-aluminic sulphate, similar in form and composition to common potash-alum, and several phosphates exactly analogous in composition to the phosphates of sodium. In most respects, however, it is more nearly allied to the heavy metals, especially to lead, which it resembles closely in appearance, density, melting point, specific heat, and electric conductivity.

Thallium Chlorides. — Thallium forms four chlorides, represented by the formulæ TlCl, Tl_4Cl_6, Tl_2Cl_4, and $TlCl_3$; the second and third of which may be regarded as compounds of the monochloride and trichloride.

The *monochloride* or *Thallious chloride*, TlCl, is formed by direct combination, the metal burning when heated in chlorine gas; or as a white curdy precipitate, resembling silver chloride, by treating the solution of any thallious salt with a soluble chloride. When boiled with water it dissolves like lead chloride, and separates in white crystals on cooling. It forms double salts with trichloride of gold and tetrachloride of platinum. The *platinum-salt*, $2TlCl.PtCl_4$, separates as a pale yellow very slightly soluble crystalline powder, on adding platinic chloride to thallious chloride.

The *trichloride* or *Thallic chloride*, $TlCl_3$, is obtained by dissolving the trioxide in hydrochloric acid, or by acting upon thallium, or one of the lower chlorides, with a large excess of chlorine at a gentle heat. It is soluble in water, and separates by evaporation in a vacuum in hydrated crystals; melts easily, and decomposes at a high temperature. It forms crystalline double salts with the chlorides of the alkali-metals.

The *sesquichloride*, $Tl_4Cl_6 = TlCl_3.3TlCl$, is produced by dissolving thallium or the monochloride in nitromuriatic acid, and separates on cooling in yellow crystalline scales. By aqueous ammonia, potash, or even by thallious oxide, it is instantly decomposed into sesquioxide and monochloride, according to the equation:

$$2Tl_4Cl_6 + 3KHO = Tl_2O_3 + 6TlCl + 3KCl + 3HCl.$$

The *dichloride*, $Tl_2Cl_4 = TlCl_3.TlCl$, is formed by carefully heating thallium, or the monochloride, in a slow current of chlorine. It is a pale-yellow substance reduced to sesquichloride by further heating.

The Bromides of thallium resemble the chlorides.

Iodides. — *Thallious iodide*, TlI, is formed by direct combination of its elements, or by double decomposition. It forms a beautiful yellow powder, rather darker than sulphur, and melting, below redness, to a scarlet liquid,

which, as the mass cools, remains scarlet for some time after solidification, then changes to bright-yellow. The dried precipitate, when spread on paper with a little gum-water, undergoes a similar but opposite change to that experienced by mercuric iodide when heated, the yellow surface when held over a flame suddenly becoming scarlet, and frequently remaining so after cooling for several days; hard friction with a glass rod, however, changes the scarlet color back to yellow. It is very slightly soluble in water, requiring, according to Crookes, 4453 parts of water at 17·2°, and 842·4 parts at 100°, to dissolve it.

Thallic iodide, $TlCl_3$, is formed by the action of thallium on iodine dissolved in ether, as a brown solution which gradually deposits rhombic prisms. It forms crystalline compounds with the iodides of the alkali-metals.

Thallium Oxides. — Thallium forms a monoxide and a trioxide.

The *monoxide*, or *Thallious oxide*, Tl_2O, constitutes the chief part of the crust which forms on the surface of the metal when exposed to the air. It may be prepared by allowing granulated thallium to oxidize in warm moist air, and then boiling with water. The filtered solution first deposits white needles of thallium carbonate, and, on further cooling, yellow needles of the hydrate, TlHO or $Tl_2O.H_2O$, which, when left over oil of vitriol in a vacuum, yields the anhydrous monoxide as a reddish-black mass retaining the shape of the crystals. It is partially reduced to metal by hydrogen at a red heat. When fused with sulphur it yields thallious sulphide. It dissolves readily in water, forming a colorless strongly alkaline solution, which re-acts with metallic salts very much like caustic potash. This solution treated with zinc, or subjected to electrolysis, yields metallic thallium.

The *trioxide*, or *Thallic oxide*, is the chief product obtained by burning thallium in oxygen gas. It is best prepared by adding potash to the solution of a thallic salt, and drying the precipitate at 260° C. (500° F.). It is also formed by electrolysis of thallious sulphate. It is a dark-red powder reduced to thallious oxide at a red heat; neutral, insoluble in water and in alkalies. Thallic hydrate, $Tl'''HO_2$, is obtained by drying the above-mentioned precipitate at 100°.

Oxygen Salts. — Both the oxides of thallium dissolve readily in acids, forming crystalline salts, soluble in water; there are also a few insoluble thallium salts formed by double decomposition.

Thallious Carbonate, CO_3Tl_2, is deposited in crystals, apparently trimetric, when a solution of thallious oxide is exposed to the air. It is soluble in water, and the solution has a slightly caustic taste and alkaline reaction.

Sulphates. — Thallious sulphate, SO_4Tl_2, obtained by evaporating the chloride or nitrate with sulphuric acid, or by heating metallic thallium with that acid, crystallizes in anhydrous rhombic prisms, isomorphous with potassium sulphate. It forms, with aluminium sulphate, the salt $(SO_4)_2Al'''Tl.12OH_2$, isomorphous with common alum; and with the sulphates of magnesium, nickel, &c., double salts containing 6 molecules of water, and isomorphous with magnesium and potassium sulphate, &c. (p. 349). — *Thallic sulphate*, $(SO_4)_3Tl_2'''.7OH_2$, separates by evaporation from a solution of thallic oxide in dilute sulphuric acid, in thin colorless laminæ, which are decomposed by water, even in the cold, with separation of brown thallic oxide.

Phosphates. — The thallious phosphates form a series nearly as complete as those of the alkali-metals, which they also resemble in their behavior when heated. There are three *orthophosphates* containing respectively PO_4H_2Tl, PO_4HTl_2, and PO_4Tl_3. The first two are soluble in water; the second is obtained by neutralizing dilute phosphoric acid at boiling heat with thal-

lious carbonate; and the first by mixing the dithallious salt with excess of phosphoric acid. The *trithallious salt*, PO_4Tl_3, is very sparingly soluble, and is formed as a crystalline precipitate on mixing the saturated solutions of ordinary disodic phosphate and thallious sulphate; also, together with ammonio-thallious phosphate, by treating the monothallious or dithallious salt with excess of ammonia. There are two *thallious pyrophosphates*, $P_2O_7H_2Tl_2$ and $P_2O_7Tl_4$, both very soluble in water: the first produced by carefully heating monothallious orthophosphate, the second by strongly heating dithallious orthophosphate. Of *thallious metaphosphate*, PO_3Tl, there are two modifications: the first remaining as a slightly soluble vitreous mass when monothallious orthophosphate is strongly ignited, the second obtained as an easily soluble glass by igniting ammonio-thallious orthophosphate.

Thallic orthophosphate, $PO_4Tl'''.2OH_2$, separates as an insoluble gelatinous precipitate on diluting a solution of thallic nitrate mixed with phosphoric acid.

Thallium Sulphide, Tl_2S. — This compound is precipitated from all thallious salts by ammonium sulphide, and from the acetate, carbonate, or oxalate, by hydrogen sulphide (incompletely also from the nitrate, sulphate or chloride), in dense flocks of a grayish or brownish-black color. Thallic salts appear to be reduced to thallious salts by boiling with ammonium sulphide. Thallium sulphate projected into fused potassium cyanide is reduced to sulphide, which then forms a brittle metallic-looking mass, having the lustre of plumbago, and fusing more readily than metallic thallium.

Reactions of Thallium salts. — The reactions of *thallious salts* with hydrogen sulphide and ammonium sulphide have just been mentioned. From their aqueous solutions thallium is rapidly precipitated in metallic crystals by *zinc*, slowly by *iron*. *Soluble chlorides* precipitate difficultly soluble white thallious chloride; soluble *bromides* throw down white, nearly insoluble bromide; soluble *iodides* precipitate insoluble yellow thallious iodide. Caustic *alkalies* and *alkaline carbonates* form no precipitate; *sodium phosphate* forms a white precipitate, insoluble in ammonia, easily soluble in acids.

Potassium chromate gives a yellow precipitate of thallious chromate, insoluble in cold nitric or sulphuric acid, but turning orange-red on boiling in the acid solution. — *Platinic chloride* precipitates a very pale-yellow insoluble double salt.

Thallic salts are easily distinguished from thallious salts by their behaviour with alkalies, and with soluble chlorides or bromides. Their solutions give with *ammonia*, and with *fixed alkalies* and their *carbonates*, a brown gelatinous precipitate of thallic oxide, containing the whole of the thallium. Soluble *chlorides* or *bromides* produce no precipitate in solutions of pure thallic salts; but if a thallious salt is likewise present, a precipitate of sesquichloride or sesquibromide is formed. *Oxalic acid* forms in solutions of thallic salts a white pulverulent precipitate; *phosphoric acid* a white gelatinous precipitate; and *arsenic acid* a yellow gelatinous precipitate. Thallic nitrate gives with *potassium ferrocyanide* a green, and with the *ferricyanide* a yellow precipitate.

In examining a mixed metallic solution, thallium will be found in the precipitate thrown down by ammonium sulphide, together with iron, nickel, manganese, &c. From these metals it may be easily separated by precipitation with potassium iodide or platinic chloride, or by reduction to the metallic state with zinc.

Thallium salts are reduced before the blowpipe with charcoal and sodium carbonate or potassium cyanide. The green color imparted to flame by thallium, and the peculiar character of its spectrum, have already been mentioned.

GOLD.

Atomic weight, 196·7. Symbol, Au (Aurum).

Gold, in small quantities, is a very widely diffused metal; traces of it are constantly found in the iron pyrites of the more ancient rocks. It is always met with in the metallic state, sometimes beautifully crystallized in the cubic form, associated with quartz, iron oxide, and other substances, in regular mineral veins. The sands of various rivers have long furnished gold derived from this source, and separable by a simple process of washing; such is the *gold-dust* of commerce. When a veinstone is wrought for gold, it is stamped to powder, and shaken in a suitable apparatus with water and mercury; an amalgam is thus formed, which is afterwards separated from the mixture and decomposed by distillation. Formerly, the chief supply of gold was obtained from the mines of Brazil, Hungary, and the Ural mountains; but California and Australia now yield by far the largest quantity. The new gold-field of British Columbia is also very productive.

Native gold is almost always alloyed with silver. The purest specimens have been obtained from Schabrowski, near Katharinenburg, in the Ural. A specimen analyzed by Gustav Rose was found to contain 98·96 per cent. of gold. The Californian gold averages from 87·5 to 88·5 per cent., and the Australian from 96 to 96·6 per cent. In some specimens of native gold, as in that from Linarowski, in the Altai mountains, the percentage of gold is as low as 60 per cent., the remainder being silver. There is also an auriferous silver found at Konigsberg, in Hungary, containing 28 per cent. of gold and 72 of silver.

Pure gold is obtained from its alloys by solution in nitro-muriatic acid and precipitation with a ferrous salt, which reduces the gold, and is itself converted into a ferric salt, thus:

$$\underset{\text{Ferrous sulphate.}}{6SO_4Fe} + \underset{\text{Auric chloride.}}{2AuCl_3} = \underset{\text{Ferric sulphate.}}{2(SO_4)_3Fe'''_2} + \underset{\text{Ferric chloride.}}{Fe'''_2Cl_6} + \underset{\text{Gold.}}{Au_2}.$$

The gold falls as a brown powder which acquires the metallic lustre by friction.

Gold is a soft metal, having a beautiful yellow color. It surpasses all other metals in malleability, the thinnest gold leaf not exceeding, it is said, $\frac{1}{200,000}$ of an inch in thickness, while the gilding on the silver wire used in the manufacture of *gold-lace* is still thinner. It may also be drawn into very fine wire. Gold has a density of 19·5: it melts at a temperature a little above the fusing point of silver. Neither air nor water affects it in the least at any temperature; the ordinary acids fail to attack it singly. A mixture of nitric and hydrochloric acids dissolves gold, however, with ease, the active agent being the liberated chlorine.

Gold forms two series of compounds: the *aurous compounds*, in which it is univalent, as AuCl, Au_2O, &c., and the *auric compound*, in which it is trivalent, as $Au'''Cl_3$, Au'''_2O_3, &c.

Chlorides. — The *monochloride* or *Aurous chloride*, AuCl, is produced when the trichloride is evaporated to dryness, and exposed to a heat of 227° C. (440° F.), until chlorine ceases to be exhaled. It forms a yellowish-white mass, insoluble in water. In contact with that liquid it is decomposed slowly in the cold, and rapidly by the aid of heat, into metallic gold and trichloride.

The *trichloride*, or *Auric chloride*, $AuCl_3$, is the most important compound of gold: it is always produced when gold is dissolved in nitro-muriatic acid.

The deep-yellow solution thus obtained yields, by evaporation, yellow crystals of the double chloride of gold and hydrogen: when this is cautiously heated, hydrochloric acid is expelled, and the residue, on cooling, solidifies to a red crystalline mass of auric chloride, very deliquescent, and soluble in water, alcohol, and ether. Auric chloride combines with a number of metallic chlorides, forming a series of double salts, called *chloro-aurates*, of which the general formula in the anhydrous state is $MCl.AuCl_3$, M representing an atom of a monad metal. These compounds are mostly yellow when in crystals, and red when deprived of water. The *ammonium salt*, $NH_4Cl.AuCl_3.OH_2$, crystallizes in transparent needles; the sodium salt, $NaCl.AuCl_3.2OH_2$, in long four-sided prisms. Auric chloride likewise forms crystalline double salts with the hydrochlorides of many organic bases.

A mixture of auric chloride with excess of acid potassium or sodium carbonate is used for gilding small ornamental articles of copper: these are cleaned by dilute nitric acid, and then boiled in the mixture for some time, by which means they acquire a thin but perfect coating of reduced gold.

Oxides. — The *monoxide*, or *Aurous oxide*, is produced when caustic potash in solution is poured upon the monochloride. It is a green powder, partly soluble in the alkaline liquid; the solution rapidly decomposes into metallic gold, which subsides, and auric oxide, which remains dissolved.

Trioxide, or *Auric oxide*, AuO_3. — When magnesia is added to auric chloride, and the sparingly soluble aurate of magnesium well washed and digested with nitric acid, auric oxide is left as an insoluble reddish-yellow powder, which when dry becomes chestnut-brown. It is easily reduced by heat, and also by mere exposure to light; it is insoluble in oxygen-acids, with the exception of strong nitric acid, insoluble in hydrofluoric acid, easily dissolved by hydrochloric and hydrobromic acids. Alkalies dissolve it freely: indeed, the acid properties of this substance are very strongly marked; it partially decomposes a solution of potassium chloride when boiled with that liquid, potassium hydrate being produced. When digested with ammonia, it yields fulminating gold consisting, according to Berzelius, of $Au_2O_3.4NH_3\,OH_2$.

The compounds of auric oxide with alkalies are called *aurates*. The *potassium salt*, $Au_2O_3.OK_2.6OH_2$, or $AuO_2K.3OH_2$, is a crystalline salt, the solution of which is sometimes used as a bath for electro-gilding. A compound of aurate and acid sulphite of potassium, or *potassium aurosulphite*, $2(AuO_2K.4SO_3HK).OH_2$, is deposited in yellow needles when potassium sulphite is added, drop by drop, to an alkaline solution of potassium aurate.

Gold shows but little tendency to form oxygen-salts. Auric oxide dissolves in strong nitric acid, but the solution is decomposed by evaporation or dilution. A *sodio-aurous hyposulphite*, $(S_2O_3)_2AuNa_3.2OH_2$, is prepared by mixing the concentrated solutions of auric chloride and sodium hyposulphite, and precipitating with alcohol. It is very soluble in water and crystallizes in colorless needles. Its solution is used for fixing daguerreotype pictures. With barium chloride, it yields a gelatinous precipitate of *bario-aurous hyposulphite*, $(S_2O_3)_4Au_2Ba''_3$.

Sulphides. — *Aurous sulphide*, Au_2S, is formed as a dark-brown, almost black precipitate when hydrogen sulphide is passed into a boiling solution of auric chloride. It forms sulphur-salts with the monosulphides of potassium and sodium. *Auric sulphide*, Au_2S_3, is precipitated in yellow flocks when hydrogen sulphide is passed into a cold dilute solution of auric chloride. Both these sulphides dissolve in ammonium sulphide.

The presence of gold in solution may be detected by the brown precipitate with *ferrous sulphate*, fusible before the blowpipe to a bead of metallic

gold; also by the brownish-purple precipitate, called "Purple of Cassius," formed when *stannous chloride* is added to dilute gold solutions. The composition of this precipitate is not exactly known, but after ignition it doubtless consists of a mixture of stannic oxide and metallic gold.* It is used in enamel painting.

Oxalic acid slowly reduces gold to the metallic state: to insure complete precipitation, the gold-solution must be digested with it for 24 hours. For the quantitative analysis of a solution containing gold and other metals, oxalic acid is in most cases a more convenient precipitant than ferrous sulphate; inasmuch as, if the quantities of the other metals are also to be determined, the presence of a large quantity of iron salt may complicate the analysis considerably.

Gold intended for coin, and most other purposes, is always alloyed with a certain proportion of silver or copper, to increase its hardness and durability: the first-named metal confers a pale greenish color. English standard gold contains $\frac{1}{12}$ of alloy, now always copper. Gold when alloyed with copper may be estimated by fusion in a cupel with lead, in the same way as in the alloy with silver. If the alloy be free from silver, the weight of the globule of gold left in the cupel will, after repeated fusions, accurately represent the quantity of gold which is present in the alloy. But if the alloy contains silver, that metal remains with the gold after cupellation. In this case the original alloy, consisting of gold, silver, and copper, is fused in the muffle together with lead and silver; the alloy of gold and silver remaining after cupellation is then boiled with nitric acid, which dissolves the silver, the gold being left behind. By treatment of the alloy of gold and silver with nitric acid, an accurate separation is obtained only when the two metals are present in certain proportions. If the alloy contains but little silver, that metal is protected from the action of the nitric acid by the gold; again, if it contains too much silver, the gold is left as a powder when the silver is dissolved out. Experience has shown that the most favorable proportions are $\frac{1}{4}$ gold to $\frac{3}{4}$ silver; the gold is then left pure, retaining the original shape of the alloy, and can be easily dried and weighed. The quantity of silver which is added to the alloy must therefore vary with the amount of gold which it contains.

Gold-leaf is made by rolling out plates of pure gold as thin as possible, and then beating them between folds of membrane with a heavy hammer, until the requisite degree or tenuity has been reached. The leaf is made to adhere to wood, &c., by size or varnish.

Gilding on copper has very generally been performed by dipping the articles into a solution of mercury nitrate, and then shaking them with a small lump of a soft amalgam of gold with that metal, which thus becomes spread over their surfaces: the articles are subsequently heated to expel the mercury, and then burnished. Gilding on steel is done either by applying a solution of auric chloride in ether, or by roughening the surface of the metal, heating it, and applying gold-leaf with a burnisher. Gilding by electrolysis — an elegant and simple method, now rapidly superseding many of the others — has already been noticed. The solution usually employed is obtained by dissolving oxide or cyanide of gold in a solution of potassium cyanide.

* Graham's Elements of Chemistry, Am. edit. p. 466.

CLASS IV.—TETRAD METALS.

GROUP I.—PLATINUM METALS.

PLATINUM.

Atomic weight, 197·4. Symbol, Pt.

PLATINUM, palladium, rhodium, iridium, ruthenium, and osmium, form a group of metals, allied in some cases by properties in common, and still more closely by their natural association. *Crude platinum*, a native alloy of platinum, palladium, rhodium, iridium, and a little iron, occurs in grains and rolled masses, sometimes of tolerably large dimensions, mixed with gravel and transported materials, on the slope of the Ural mountains, in Russia, in Brazil, and Ceylon, and in a few other places. It has never been seen in the rock, which, however, is judged from the accompanying materials to have been serpentine. It is stated to be always present in small quantities with native silver.

From this substance platinum is prepared by the following process: The crude metal is acted upon as far as possible by nitro-muriatic acid, containing an excess of hydrochloric acid and slightly diluted with water, in order to dissolve as small a quantity of iridium as possible: to the deep yellowish-red and highly acid solution thus produced, sal-ammoniac is added, by which nearly the whole of the platinum is thrown down in the state of ammonium platinochloride. This substance, washed with a little cold water, dried, and heated to redness, leaves metallic platinum in the spongy state. This metal cannot be fused into a compact mass by ordinary furnace-heat, but the same object may be accomplished by taking advantage of its property of welding, like iron, at a high temperature. The spongy platinum is made into a thin uniform paste with water, introduced into a slightly conical mould of brass, and subjected to a graduated pressure, by which the water is squeezed out, and the mass rendered at length sufficiently solid to bear handling. It is then dried, very carefully heated to whiteness, and hammered, or subjected to powerful pressure. If this operation is properly conducted, the platinum will then be in a state to bear forging into a bar, which can afterwards be rolled into plates, or drawn into wire, at pleasure.

A method for refining platinum has lately been proposed by MM. Deville and Debray.* It consists in submitting the crude metal to the action of an intensely high temperature in a crucible of lime. The apparatus they employ is as follows: The lower part of the furnace consists of a piece of lime, hollowed out in the centre to the depth of about a quarter of an inch; a small notch is filed at one side of this basin, through which the metal is introduced and poured out. A cover made of another piece of lime fits on the top of this basin: it is also hollowed to a small extent, and has a conical perforation at the top, into which is inserted the nozzle of an oxyhydrogen blowpipe. The whole arrangement is firmly bound with iron wire. To use the apparatus, the stopcock supplying the hydrogen (or coal gas) is opened and the gas lighted at the notch in the crucible: the oxygen

* Ann. Chim. Phys. [3] lvi. 385.

is then gradually supplied; and when the furnace is sufficiently hot, the metal is introduced in small pieces through the orifice. By this arrangement as much as 50 pounds of platinum and more may be fused at once. All the impurities in the platinum, except the iridium and rhodium, are separated in this manner: the gold and palladium are volatilized; the sulphur, phosphorus, arsenic, and osmium, oxidized and volatilized; and the iron and copper oxidized and absorbed by the lime of the crucible.

Platinum is a little whiter than iron: it is exceedingly malleable and ductile, both hot and cold, and is very infusible, melting only before the oxy-hydrogen blowpipe, or in the powerful blast-furnace just described. It is the heaviest substance known, its specific gravity being 21·5. Neither air, moisture, nor the ordinary acids attack platinum in the slightest degree at any temperature: hence its great value in the construction of chemical vessels. It is dissolved by nitro-muriatic acid, and superficially oxidized by fused potassium hydrate, which enters into combination with the oxide.

The remarkable property of the spongy metal to determine the union of oxygen and hydrogen has been already noticed. There is a still more curious state in which platinum can be obtained — that of *platinum-black*, in which the division is carried much further. It is easily prepared by boiling a solution of platinic chloride, to which an excess of sodium carbonate and a quantity of sugar have been added, until the precipitate formed after a little time becomes perfectly black, and the supernatant liquid colorless. The black powder is collected on a filter, washed and dried by gentle heat. This substance appears to possess the property of condensing gases, more especially oxygen, into its pores to a very great extent; when placed in contact with a solution of formic acid, it converts the latter, with copious effervescence, into carbonic acid; alcohol, dropped upon the platinum-black, becomes changed by oxidation to acetic acid, the rise of temperature being often sufficiently great to cause inflammation. When exposed to a red-heat, the black substance shrinks in volume, assumes the appearance of common spongy platinum, and loses these peculiarities, which are no doubt the result of its excessively comminuted state.

Platinum forms two series of compounds: the *platinous compounds*, in which it is bivalent, *e.g.* $Pt''Cl_2$, $Pt''O$, and the *platinic compounds*, in which it is quadrivalent, *e.g.*, $Pt^{iv}Cl_4$, $Pt''O_2$, &c.

Chlorides. — The *dichloride*, or *Platinous chloride*, $Pt''Cl_2$, is produced when platinic chloride, dried and powdered, is exposed for some time to heat of about 200°, whereby half the chlorine is expelled; also, when sulphurous acid gas is passed into a solution of the tetrachloride until the latter ceases to give a precipitate with sal-ammoniac. It is a-greenish-gray powder, insoluble in water, but dissolved by hydrochloric acid. The latter solution, mixed with sal-ammoniac or potassium chloride, deposits a double salt in fine red prismatic crystals, containing, in the last case, $2KCl.PtCl_2$. The corresponding sodium-compound is very soluble and difficult to crystallize. These double salts are called *platinoso-chlorides* or *chloroplatinites*. Platinous chloride is decomposed by heat into chlorine and metallic platinum.

The *tetrachloride*, or *Platinic chloride*, $Pt^{iv}Cl_4$, is always formed when platinum is dissolved in nitro-muriatic acid. The acid solution yields, on evaporation to dryness, a red or brown residue, deliquescent, and very soluble both in water and in alcohol; the aqueous solution has a pure orange-yellow tint. Platinic chloride unites with a great variety of metallic chlorides, forming double salts called *platino-chlorides* or *chloro-platinates*; the most important of these compounds are those containing the metals of the alkalies and ammonium. *Potassium platinochloride*, $2KCl.PtCl_4$, forms a bright yellow crystalline precipitate, being produced whenever solutions of the chlorides of platinum and of potassium are mixed, or a potassium

salt mixed with a little hydrochloric acid is added to platinum tetrachloride. It is feebly soluble in water, still less soluble in dilute alcohol, and is decomposed with some difficulty by heat. It is easily reduced by hydrogen at a high temperature, yielding a mixture of potassium chloride and platinum-black: the latter substance may thus, indeed, be very easily prepared. The *sodium-salt*, $2NaCl.PtCl_4.6OH_2$, is very soluble, crystallizing in large, transparent, yellow-red prisms of great beauty. The *ammonium-salt*, $2NH_4Cl.PtCl_4$, is undistinguishable, in physical characters, from the potassium-salt; it is thrown down as a precipitate of small, transparent, yellow, octohedral crystals when sal-ammoniac is mixed with platinic chloride; it is but feebly soluble in water, still less so in dilute alcohol, and is decomposed by heat, yielding spongy platinum, while sal-ammoniac, hydrochloric acid, and nitrogen are driven off. Platinic chloride also forms crystallizable double salts with the hydrochlorides of many organic bases; with ethylamine, for example, the compound, $2[NH_2(C_2H_5)HCl].PtCl_4$.

The *bromides* and *iodides of platinum* are analogous in composition to the *chlorides*, and likewise form double salts with alkaline bromides and iodides.

Oxides. — The *monoxide*, or *Platinous oxide*, $Pt''O$, is obtained by digesting the dichloride with caustic potash, as a black powder, soluble in excess of alkali. It dissolves also in acids with brown color, and the solutions are not precipitated by sal-ammoniac. When platinum dioxide is heated with solution of oxalic acid, it is reduced to monoxide, which remains dissolved. The liquid has a dark-blue color, and deposits fine copper-red needles of platinous oxalate.

The *dioxide*, or *Platinic oxide*, $Pt^{iv}O_2$, is best prepared by adding barium nitrate to a solution of platinic sulphate; barium sulphate and platinic nitrate are then produced, and from the latter caustic soda precipitates one half of the platinum as *platinic hydrate*. The sulphate is itself obtained by acting with strong nitric acid upon platinum bisulphide, which falls as a black powder when a solution of the tetrachloride is dropped into potassium sulphide. Platinic hydrate is a bulky brown powder, which, when gently heated, becomes black and anhydrous. It may also be formed by boiling platinic chloride with a great excess of caustic soda, and then adding acetic acid. It dissolves in acids, and also combines with bases: the salts have a yellow or red tint, and a great disposition to unite with salts of the alkalies and alkaline earths, giving rise to a series of double compounds, which are not precipitated by excess of alkali. A combination of platinic oxide with ammonia exists, which is explosive. Both oxides of platinum are reduced to the metallic state by ignition.

Sulphides. — The compounds $Pt''S$ and $Pt^{iv}S_2$ are produced by the action of hydrogen sulphide, or the sulph-hydrate of an alkali-metal, on the dichloride and tetrachloride of platinum respectively; they are both black substances, insoluble in water. Platinic sulphide heated in a close vessel gives off half its sulphur and is reduced to platinous sulphide. It dissolves in alkaline hydrates, carbonates, and sulphides, forming salts called *sulphoplatinates*, which are decomposed by acids.

Ammoniacal Platinum Compounds.

The chlorides, oxides, sulphates, &c., of platinum are capable of taking up two or more molecules of ammonia, and forming compounds analogous in many respects to the ammoniacal mercury compounds already described. There are five series of these compounds, which may be formulated as in the following table, the symbol R denoting a univalent chlorous radical, such as Cl, Br, NO_3, &c.

I.	Diammonio-platinous compounds	. $2NH_3.Pt''R_2$.
II.	Tetrammonio-platinous compounds	. $4NH_3.Pt''R_2$.
III.	Diammonio-platinic compounds	. $2NH_3.Pt^{iv}R_4$.
IV.	Tetrammonio-platinic compounds	. $4NH_3.Pt^{iv}R_4$.
V.	Octammonio-diplatinic compounds	. $8NH_3.Pt^{iv}_2R_6O''$.

Any number of atoms of the univalent radical R may be replaced in these compounds by an equivalent quantity of another radical, univalent or multivalent, thus giving rise to oxychlorides, nitrato-chlorides, oxynitrates, &c.

The *diammonio-platinous* and *tetrammonio-platinic compounds* (I. and IV.) may evidently be derived from double and quadruple molecules of ammonium salts, by the substitution of Pt'' or Pt^{iv} for an equivalent quantity of hydrogen: *e. g.*, $2NH_3.Pt''Cl_2=(N_2H_6Pt'').Cl_2$; and $4NH_3.Pt^{iv}Cl_4=(N_4H_{12}Pt^{iv}).Cl_4$. The composition of the *tetrammonio-platinous compounds* (II.) will be understood when it is remembered that, nitrogen being a pentad element, NH_3, is a bivalent radical, and that any number of such radicals may be added to a compound without disturbing the balance of equivalency (pp. 234, 235). Further, since the addition of NH_3 to any compound containing hydrogen comes to the same thing as replacing an atom of hydrogen in that compound by ammonium, NH_4, these tetrammonio-platinous compounds may also be regarded as salts of *diammoplatoso-diammonium*, that is, of a double ammonium molecule, N_2H_8, in which two atoms of hydrogen are replaced by Pt'', and two more by $(NH_4)_2$. — In the *diammonio-platinic compounds* (III.), the bivalent radical $(Pt^{iv}Cl_2)''$ plays the same part as Pt'' in the diammonio-platinous compounds.

The following table exhibits the constitution of the several groups of compounds according to these views, taking the chlorides as examples:

I. $2NH_3.PtCl_2 = (N_2H_6Pt'')Cl_2 = \begin{matrix} NH_3Cl \\ | \\ Pt \\ | \\ NH_3Cl \end{matrix}$

II. $4NH_3.Pt''Cl_2 = [N_2H_4(NH_4)_2Pt'']Cl_2 = \begin{matrix} NH_3Cl \\ | \\ NH_3 \\ | \\ Pt \\ | \\ NH_3 \\ | \\ NH_3Cl \end{matrix}$

III. $2NH_3.Pt^{iv}Cl_4 = [N_2H_6(Pt^{iv}Cl_2)'']Cl_2 = \begin{matrix} NH_3Cl \\ | \\ PtCl_2 \\ | \\ NH_3Cl \end{matrix}$

IV. $4NH_3.Pt^{iv}Cl_4 = (N_4H_{12}Pt^{iv})Cl_4 = \begin{matrix} N_2H_6Cl_2 \\ \| \\ Pt \\ \| \\ N_2H_6Cl_2. \end{matrix}$

V. The *octammonio-diplatinic compounds* consist of double molecules of tetrammonio-platinic compounds having two or more molecules of the uni-

valent radical R, replaced by an equivalent quantity of a bivalent radical: *e. g.*, the *oxynitrate* $= 8NH_3.Pt^{iv}_2(NO_3)_6O'' = (N_8H_{24}Pt^{iv}_2)\left\{\begin{matrix}(NO_3)_6\\O''\end{matrix}\right.$.

I. *Diammonio-platinous Compounds.* — These compounds are formed by the action of heat on those of the following series, half the ammonia of the latter being then given off. They are for the most part insoluble in water, but dissolve in ammonia, reproducing the tetrammonio-platinous compounds: they detonate when heated.

Chloride, $N_2H_6Pt''Cl_2$. — Of this compound there are three isomeric modifications: — *α. Yellow*, obtained by adding hydrochloric acid, or a soluble chloride, to a solution of diammonio-platinous nitrate or sulphate, or by boiling the green modification, *γ*, with ammonium nitrate or sulphate; or, by neutralizing a solution of platinous chloride in hydrochloric acid with ammonium carbonate, heating the mixture to the boiling point, and adding a quantity of ammonia equal to that already contained in the liquid, filtering from a dingy green substance, which deposits after a while, then leaving the solution to cool, and decanting the supernatant liquid as soon as the yellow salt is deposited. *β. Red.* — If, in the last mode of preparation, the ammonium carbonate, instead of being added at once in excess, be added drop by drop to the hydrochloric acid solution of platinous chloride, the liquid on cooling deposits small garnet-colored crystals having the form of six-sided tables. This red modification may also be obtained in other ways. *γ. Green.* — This modification, usually denominated the *green salt of Magnus*, was the first discovered of the ammoniacal platinum compounds. It is obtained by gradually adding an acid solution of platinous chloride to caustic ammonia; or by passing sulphurous acid gas into a boiling solution of platinic chloride, till it is completely converted into platinous chloride (and therefore no longer gives a precipitate with sal-ammoniac), and neutralizing the solution with ammonia; the compound is then deposited in green needles. The same modification of the salt may also be obtained by adding an acid solution of platinous chloride to a solution of tetrammonio-platinous chloride, $N_4H_{12}Pt''Cl_2$. The corresponding *iodide*, $N_2H_6Pt''I_2$, is a yellow powder, obtained by heating the aqueous solution of the compound, $N_4H_{12}Pt''I_2$. It dissolves in ammonia, reproducing the latter compound. The *oxide*, $N_2H_6Pt''O$, obtained by heating tetrammonio-platinous hydrate to 110°, is a grayish mass, which, when heated to 100° in a close vessel, gives off water, ammonia, and nitrogen, and leaves metallic platinum. The *sulphate*, $N_2H_6Pt''SO_4.OH_2$, and the *nitrate*, $N_2H_6Pt''(NO_3)_2$, are obtained by boiling the iodide with sulphate and nitrate of silver: they are crystalline and have a strong acid reaction. The sulphate retains a molecule of crystallization-water, which cannot be removed without decomposing the salt.

II *Tetrammonio-platinous Compounds.* — The *chloride*, $N_4H_{12}Pt''Cl_2$, is prepared by boiling platinous chloride, or the green salt of Magnus, with aqueous ammonia till the whole is dissolved, and evaporating the liquid to the crystallizing point. The *bromide* and *iodide* of this series are obtained by treating the solution of the sulphate with bromide or iodide of barium: they crystallize in cubes. The *oxide*, $N_4H_{12}Pt''O$, is obtained as a crystalline mass by decomposing the solution of the sulphate with an equivalent quantity of baryta-water, and evaporating the filtrate in a vacuum. It is strongly alkaline and caustic, like potash, absorbs carbonic acid rapidly from the air, and precipitates silver oxide from the solution of the nitrate. It is a strong base, neutralizing acids completely, and expelling ammonia from its salts. It melts at 110°, giving off water and ammonia, and leaving diammonio-platinous oxide. Its aqueous solution does not give off ammonia, even when boiled.

Carbonates.—The oxide absorbs carbon dioxide rapidly from the air, forming first a neutral carbonate, $N_4H_{12}Pt''CO_3.OH_2$, and afterwards an

acid salt, $N_4H_{12}Pt''CO_3.CO_3H_2$. The *sulphate*, $N_4H_{12}Pt''SO_4$, and the *nitrate*, $N_4H_{12}Pt''(NO_3)_2$, are obtained by decomposing the chloride with silver sulphate or nitrate; they are neutral, and crystallize easily.

III. *Diammonio-platinic Compounds.*—The *chloride*, $N_2H_6Pt^{iv}Cl_4$, is obtained by passing chlorine gas into boiling water in which diammonio-platinous chloride (the yellow modification) is suspended. This compound is insoluble in cold water, and very slightly soluble in boiling water, or in water containing hydrochloric acid. It dissolves in ammonia at a boiling heat, and the solution, on cooling, deposits a yellow precipitate, consisting of tetrammoniacal platinic chloride. It dissolves in boiling potash without evolving ammonia.

Nitrates.—An *oxynitrate*, $N_2H_6Pt^{iv}(NO_3)_2O''$, is obtained by boiling the chloride, $N_2H_6PtCl_4$, for several hours with a dilute solution of silver nitrate. It is a yellow crystalline powder, sparingly soluble in cold, more soluble in boiling water. The *normal nitrate*, $N_2H_6Pt^{iv}(NO_3)_4$, is obtained by dissolving the oxynitrate in nitric acid: it is yellowish, insoluble in cold water, soluble in hot nitric acid.

The *oxide*, $N_2H_6Pt^{iv}O_2$, is obtained by adding ammonia to a boiling solution of diammonio-platinic nitrate; it is then precipitated in the form of a heavy yellowish, crystalline powder, composed of small shining rhomboïdal prisms; it is nearly insoluble in boiling water, and resists the action of boiling potash. Heated in a close vessel, it gives off water and ammonia, and leaves metallic platinum. It dissolves readily in dilute acids, even in acetic acid, and forms a large number of crystallizable salts, both neutral and acid, having a yellow color, and sparingly soluble in water.* Another compound of platinic oxide with ammonia, called *fulminating platinum*, whose composition has not been exactly ascertained, is produced by decomposing ammonium platino-chloride with aqueous potash. It is a straw-colored powder, which detonates slightly when suddenly heated, but strongly when exposed to a gradually increasing heat.

IV. *Tetrammonio-platinic Compounds.*—The oxide of this series has not yet been isolated. The *chloride*, $N_4H_{12}Pt^{iv}Cl_4$, is obtained by passing chlorine gas into a solution of tetrammonio-platinous chloride; by dissolving diammonio-platinic chloride in ammonia, and expelling the excess of ammonia by evaporation; or by precipitating a solution of tetrammonio-platinic oxynitrate or nitrato-chloride with hydrochloric acid. It is white, and dissolves in small quantity in boiling water, from which solution it is deposited in the form of transparent regular octohedrons, having a faint yellow tint. When a solution of this salt is treated with silver nitrate, one-half of the chlorine is very easily precipitated, but to remove even a small portion of the remainder requires a long-continued action of the silver-salt. The *chlorobromide*, $N_4H_{12}Pt^{iv}Br_2Cl_2$, is prepared by treating tetrammonio-platinous chloride with bromine. An *oxynitrate*, $N_4H_{12}Pt^{iv}(NO_3)_2O$; a *nitrato-chloride*, $N_4H_{12}Pt^{iv}(NO_3)_2Cl_2$; a *sulphato-chloride*, $N_2H_{12}Pt^{iv}(SO_4)''Cl_2$; and an *oxalo-chlorule*, $N_4H_{12}Pt^{i}(C_2O_4)''Cl_2$, have likewise been obtained.

V. *Octammonio-diplatinic Compounds.* An *oxynitrate* or *basic nitrate*, $N_8H_{24}Pt^{iv}_2(NO_3)_6O''$, is produced by boiling tetrammonio-platinous nitrate with nitric acid. It is a colorless, crystalline, detonating salt, slightly soluble in cold water, more soluble in boiling water, insoluble in nitric acid. (Gerhardt.) A *nitrat-ozychloride*, $N_8H_{24}Pt^{iv}_2(NO_3)_4O''Cl_2$, discovered by Raewsky, is formed when Magnus's green salt is boiled with a large excess of nitric acid. Red fumes are then evolved, and the resulting solution de-

* Gerhardt, Comtes rendus des travaux en Chimie, 1849, p. 273.

posits the nitrat-oxychloride in small brilliant needles, which deflagrate when heated, giving off water and sal-ammoniac, and leaving metallic platinum. The nitric acid in this salt may be replaced by an equivalent quantity of carbonic or oxalic acid, yielding the compounds, $N_8H_{24}Pt^{iv}{}_2(CO_3)''{}_2O''Cl_2$, and $N_8H_{24}Pt^{iv}{}_2(C_2O_4)''{}_2O''Cl_2$, both of which are crystallizable and sparingly soluble. A *basic oxalo-nitrate*, $N_8H_{24}Pt^{iv}{}_2(C_2O_4)''{}_2(NO_3)_2O''$, insoluble in water, is obtained by adding ammonium oxalate to the oxynitratet (Gerhardt.)

Reactions of Platinum Salts.—Platinic chloride or a platinic oxygen-salt may be recognized in solution by the yellow precipitate with *sal-ammoniac*, decomposable by heat, with production of spongy metal.

Hydrogen sulphide and *ammonium sulphide* gradually form a brown precipitate of platinic sulphide, soluble in excess of ammonium sulphide. *Zinc* precipitates metallic platinum.

Platinic chloride and sodium platinochloride are employed in analytical investigations to detect the presence of potassium, and separate it from sodium. For the latter purpose, the alkaline salts are converted into chlorides, and in this state mixed with four times their weight of sodium platinochloride in crystals, the whole being dissolved in a little water. When the formation of the yellow salt appears complete, alcohol is added, and the precipitate collected on a weighed filter, washed with weak spirit, carefully dried, and weighed. The potassium chloride is then easily reckoned from the weight of the double salt; and this, subtracted from the weight of the mixed chlorides employed, gives that of the sodium chloride by difference; 100 parts of potassium platinochloride correspond to 30·51 parts of potassium chloride.

Capsules and crucibles of platinum are of great value to the chemist: the latter are constantly used in mineral analysis for fusing siliceous matter with alkaline carbonates. They suffer no injury in this operation, although caustic alkali roughens and corrodes the metal. The experimenter must be particularly careful to avoid introducing any oxide of an easily fusible metal, as that of lead or tin, into a platinum crucible. If reduction should by any means occur, these metals will at once alloy themselves with the platinum, and the vessel will be destroyed. A platinum crucible must never be put naked into a coke or charcoal fire, but always placed within a covered earthen crucible.

PALLADIUM.

Atomic weight, 106·5. Symbol, Pd.

When the solution of crude platinum, from which the greater part of that metal has been precipitated by sal-ammoniac, is neutralized by sodium carbonate, and mixed with a solution of mercuric cyanide, palladium cyanide separates as a whitish insoluble substance, which, on being washed, dried, and heated to redness, yields metallic palladium in a spongy state. The palladium may then be welded into a mass, in the same manner as platinum.

Palladium closely corresponds with platinum in color and appearance; it is also very malleable and ductile. Its density differs very much from that of platinum, being only 11·8. Palladium is more oxidable than platinum. When heated to redness in the air, especially in the state of sponge, it acquires a blue or purple superficial film of oxide, which is again reduced at a white heat. This metal is slowly attacked by nitric acid; its best solvent is nitro-muriatic acid.

Palladium, like platinum, forms two classes of compounds; namely, the *palladious compounds*, in which it is bivalent, and the *palladic compounds*, in which it is quadrivalent.

Chlorides. — The *dichloride*, or *Palladious chloride*, $Pd''Cl_2$, is obtained by dissolving the metal in nitro-muriatic acid, and evaporating the solution to dryness. It is a dark-brown mass, which dissolves in water if the heat has not been too great, and forms double salts with many metallic chlorides. The palladio-chlorides of ammonium and potassium are much more soluble than the corresponding platino-chlorides: they have a brownish-yellow tint.

The *tetrachloride*, or *Palladic chloride*, $Pd^{iv}Cl_4$, exists only in solution and in combination with the alkaline chlorides. It is formed when the dichloride is digested in nitro-muriatic acid. The solution has an intense brown color, and is decomposed by evaporation. Mixed with potassium chloride, or sal-ammoniac, it gives rise to a red crystalline precipitate, which is but little soluble in water.

Palladious Iodide, $Pd''I_2$, is precipitated from the chloride or nitrate by soluble iodides, as a black mass, which gives off its iodine between 300° and 360° C. (572° and 680° F.) Palladium-salts are employed for the quantitative estimation of iodine, chlorine and bromine not being precipitated by them.

Oxides. — The *monoxide*, or *Palladious oxide*, $Pd''O$, is obtained by evaporating to dryness, and cautiously heating, the solution of palladium in nitric acid. It is black, and but little soluble in acids. The hydrate falls as a dark-brown precipitate when sodium carbonate is added to the above solution. It is decomposed by a strong heat.

The *dioxide*, or *Palladic oxide*, $Pd^{iv}O^2$, is not known in the separate state. From a solution of palladic chloride, alkalies and alkaline carbonates throw down a brown precipitate consisting of hydrated palladic oxide combined with the alkali. This compound gives off half its oxygen at a moderate heat, and the whole at a higher temperature. From hot solutions, a black precipitate is obtained containing the anhydrous dioxide. The hydrate dissolves slowly in acids, forming yellow solutions. In strong hydrochloric acid it dissolves without decomposition, forming *potassio-palladic chloride*, arising from admixed potash; with dilute hydrochloric acid, on the contrary, it gives off chloride.

Palladious Sulphide, $Pd''S$, is formed by fusing the metal with sulphur, or by precipitating a solution of a palladious salt with hydrogen sulphide. It is insoluble in ammonium sulphide.

Ammoniacal Palladium Compounds. — A moderately concentrated solution of palladium dichloride treated with a slight excess of ammonia, yields a beautiful flesh-colored or rose-colored precipitate, consisting of $N_2H_6Pd''Cl_2$. This precipitate dissolves in a larger excess of ammonia; and the ammoniacal solution, when treated with acids, yields a yellow precipitate having the same composition. This yellow modification is likewise obtained by heating the red compound in the moist state to 100°, or in the dry state to 200° C. (392° F.) The yellow compound dissolves abundantly in aqueous potash, forming a yellow solution, but without giving off ammonia, even when the liquid is heated to the boiling-point; the red compound behaves in a similar manner, but, before dissolving, is converted into the yellow modification. For this reason, Hugo Müller regards the red compound as *palladium ammonio-chloride*, $2NH_3.Pd''Cl_2$, and the yellow as *palladammonium chloride*, $N_2H_6Pd''Cl_2$. The yellow compound, digested with water and silver oxide, yields *palladammonium oxide*, $N_2H_6Pd''O$, which is a strong base, soluble in

water, having an alkaline taste and reaction, and absorbing carbonic acid from the air. *Palladammonium sulphite*, $N_2H_6Pd''.SO_3$, is formed by the action of sulphurous acid on the oxide or chloride; it crystallizes in orange-yellow octohedrons. The *sulphite*, *chloride*, *iodide*, and *bromide*, have likewise been formed.

The *compound*, $4NH_3.Pd''Cl_2$, or *ammopalladammonium chloride*, $[N_2H_4Pd''(NH_4)_2]''Cl_2$, separates from an ammoniacal solution of palladammonium chloride in oblique rhombic prisms.

The *oxide*, $N_4H_{12}Pd''O$, obtained by decomposing the solution of this chloride with silver oxide, is also a strong base yielding crystallizable salts.*

Palladious salts are well marked by the pale yellowish-white precipitate with solution of mercuric cyanide. It consists of palladious cyanide, $Pd''Cy_2$, and is converted by heat into the spongy metal.

Hydriodic acid and *potassium iodide* throw down a black precipitate of palladium iodide, visible even to the 500,000th degree of dilution.

Palladium is readily alloyed with other metals, as copper; one of these compounds—namely, the alloy with silver—has been applied to useful purposes. An amalgam of palladium is now extensively used by dentists for stopping teeth.

A native alloy of gold with palladium is found in Brazil.

RHODIUM.

Atomic weight, 104. Symbol, Rh.

The solution from which platinum and palladium have been separated, in the manner already described, is mixed with hydrochloric acid, and evaporated to dryness. The residue is treated with alcohol of specific gravity 0·837, which dissolves everything except the double chloride of rhodium and sodium. This is well washed with spirit, dried, heated to whiteness, and then boiled with water, whereby sodium chloride is dissolved out, and metallic rhodium remains. Thus obtained, rhodium is a white, coherent, spongy mass, more infusible and less capable of being welded than platinum. Its specific gravity varies from 10·6 to 11.

Rhodium is very brittle: reduced to powder and heated in the air, it becomes oxidized, and the same alteration happens to a greater extent when it is fused with nitrate or bisulphate of potassium. None of the acids, singly or conjoined, dissolve this metal, unless it be in the state of alloy, as with platinum, in which state it is attacked by nitro-muriatic acid.

Rhodium forms but one chloride, containing $RhCl_3$: hence it might be supposed to be a triad; but, from its analogy to the other platinum metals, it is generally regarded as a tetrad, the chloride just mentioned being represented by the formula Rh_2Cl_6, or $\left|\begin{matrix}RhCl_3\\RhCl_3\end{matrix}\right.$.

This chloride is prepared by adding silicofluoric acid to the double chloride of rhodium and potassium, evaporating the filtered solution to dryness, and dissolving the residue in water. It forms a brownish-red deliquescent mass, soluble in water, with a fine red color. It is decomposed by heat into chlorine and metallic rhodium.

Rhodium and Potassium chlorides.—The salt, $Rh_2Cl_6.6KCl.6OH_2$, formed by

* Hugo Müller, Ann. Ch. Pharm. lxxxvi. 341.

mixing a solution of rhodic oxide in hydrochloric acid with a strong solution of potassium chloride, crystallizes in sparingly soluble efflorescent prisms. Another double salt containing $Rh_2Cl_6.4KCl.2OH_2$, is prepared by heating in a stream of chlorine a mixture of equal parts of finely powdered metallic rhodium and potassium chloride. The salt has a fine red color, is soluble in water, and crystallizes in four-sided prisms *Rhodium and sodium chloride*, $Rh_2Cl_6.6NaCl.24OH_2$, is also a very beautiful red salt, prepared like the last. The *ammonium salt*, $Rh_2Cl_6.6NH_4Cl.3OH_2$, obtained by decomposing the sodium salt with sal-ammoniac, crystallizes in fine rhombohedral prisms.

Rhodium Oxides. — Rhodium forms four oxides, containing RhO, Rh_2O_3, RhO_2, and RhO_3.

The *monoxide*, RhO, is formed, with incandescence, when the hydrated sesquioxide, $Rh_2O_3.3OH_2$, is heated in a platinum crucible. It is a dark-gray substance, perfectly indifferent to acids.

The *sesquioxide* or *rhodic oxide*, Rh_2O_3, obtained by heating the nitrate, is a gray porous mass, with metallic iridescence; insoluble in acids, easily reduced by hydrogen. It forms two hydrates: $Rh_2O_3.3OH_2$, or RhH_3O_3, obtained by precipitating a solution of rhodium and sodium chloride with potash in presence of alcohol, and $Rh_2O_3.5OH_2$ or $RhH_3O_3.OH_2$, formed by precipitating the same salt with aqueous potash.

The *dioxide*, RhO_2, obtained by fusing pulverized rhodium or the sesquioxide with nitre and potash, and digesting the fused mass with nitric acid, to dissolve off the potash, is a dark-brown substance, insoluble in acids. When chlorine is passed into a solution of rhodic pentahydrate, $Rh_2O_3.5OH_2$, a black-brown gelatinous precipitate of the trihydrate, $Rh_2O_3.3OH_2$, is formed at first; but this compound gradually loses its gelatinous consistence, becomes lighter in color, and is finally converted into a green hydrate of the dioxide, $RhO_2.2OH_2$. The alkaline solution at the same time acquires a deep violet-blue color.

Trioxide, RhO_3. — The blue alkaline solution above mentioned, deposits, after a while, a blue powder, becoming green when dry, and yielding, when treated with nitric acid, a blue flocculent substance, consisting of the trioxide, easily reduced to the dioxide.

Rhodic Sulphate, $(SO_4)_3Rh_2.12OH_2$, formed by oxidizing the sulphide with nitric acid, is a yellowish-white crystalline mass. *Potassio-rhodic sulphate*, $(SO_4)_3RhK_3$, is a reddish-yellow crystalline powder formed by adding sulphuric acid to a solution of rhodium and potassium chloride.

Ammoniacal Rhodium Compounds. — An *ammonio-chloride*, $10NH_3.Rh_2Cl_6$, or $[N_6H_{14}Rh'''_2(NH_4)_4]^{vi}Cl_6$, is obtained as a yellow crystalline powder on mixing a dilute solution of rhodium and ammonium chloride with excess of ammonia, and leaving the filtered solution to evaporate. The corresponding oxide, $10NH_3.Rh_2O_3$, obtained by heating the chloride with silver oxide, is a strong base, from which the sulphate and oxalate may be obtained in crystalline form.

Rhodic salts are, for the most part, rose-colored, and exhibit, in solution, the following reactions: with *hydrogen sulphide*, and *ammonium sulphide*, a brown precipitate of rhodic sulphide, insoluble in excess of ammonium sulphide; with soluble *sulphites*, a pale-yellow precipitate, affording a characteristic reaction; with *potash*, a yellow precipitate of rhodic oxide, soluble in excess; with *ammonia* and with *alkaline carbonates*, a yellow precipitate after a while. No precipitate with alkaline chlorides or mercuric cyanide. *Zinc* precipitates metallic rhodium.

An alloy of steel with a small quantity of rhodium is said to possess extremely valuable properties.

IRIDIUM.

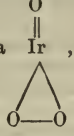
Atomic weight, 198. Symbol, Ir.

When crude platinum is dissolved in nitromuriatic acid, a small quantity of a gray scaly metallic substance usually remains behind, having altogether resisted the action of the acid: this is a native alloy of iridium and osmium, called *osmiridium* or *iridosmine;* it is reduced to powder, mixed with an equal weight of dry sodium chloride, and heated to redness in a glass tube, through which a stream of moist chlorine gas is transmitted. The farther extremity of the tube is connected with a receiver containing solution of ammonia. The gas, under these circumstances, is rapidly absorbed, iridium chloride and osmium chloride being produced: the former remains in combination with the sodium chloride; the latter, being a volatile substance, is carried forward into the receiver, where it is decomposed by the water into osmic and hydrochloric acids, which combine with the alkali. The contents of the tube when cold are treated with water, by which the iridium and sodium chloride is dissolved out: this is mixed with an excess of sodium carbonate and evaporated to dryness. The residue is ignited in a crucible, boiled with water, and dried; it then consists of a mixture of ferric oxide and a combination of iridium oxide with soda: it is reduced by hydrogen at a high temperature, and treated successively with water and strong hydrochloric acid, by which the alkali and the iron are removed, while metallic iridium is left in a finely divided state. By strong pressure and exposure to a white heat, a certain degree of compactness may be communicated to the metal.*

Iridium is a white brittle metal, fusible with great difficulty before the oxy-hydrogen blowpipe. Deville and Debray, by means of their powerful oxy-hydrogen blast furnace, have fused it completely into a pure white mass, resembling polished steel, brittle in the cold, somewhat malleable at a red heat, and having a density equal to that of platinum, viz. 21·15, (21·8 Hare.) By moistening the pulverulent metal with a small quantity of water, pressing it tightly, first between filtering paper, then very forcibly in a press, and calcining it at a white heat in a forge-fire, it may be obtained in the form of a compact, very hard mass, capable of taking a good polish, but still very porous, and of a density not exceeding 16·0. After strong ignition it is insoluble in all acids, but when reduced by hydrogen at low temperatures, it oxidizes slowly at a red heat, and dissolves in nitro-muriatic acid. It is usually rendered soluble by fusing it with nitre and caustic potash, or by mixing it with common salt, or better, with a mixture of the chlorides of potassium and sodium, and igniting it in a current of chlorine, as above described.

Iridium forms three series of compounds, namely, the *hypoiridious* compounds, in which it is bivalent, as $Ir''Cl_2$, IrO; the *iridious* compounds, in which it is quadrivalent, but apparently trivalent, *e. g.*, $Ir_2Cl_6 = \left|\begin{matrix}IrCl_3\\IrCl_3\end{matrix}\right.$, and the *iridic* compounds, in which it is also quadrivalent, as in $IrCl_4$, IrO_2,

* Osmiridium, however, generally contains platinum, ruthenium, and other metals of the same group, which are not effectually separated by the method above described. The complete separation of the several metals of the platinum group has of late years formed the subject of several elaborate investigations, into which the limits of this work will not permit us to enter. (See Watts's Dictionary of Chemistry, iii. 35; iv. 241, 680; v. 101, 124.)

&c. It appears to be incapable of uniting with more than four atoms of a monad element, and is therefore regarded as a tetrad.* It forms also a trioxide, IrO_3, in which it is apparently sexvalent, but the oxide may be represented by the formula  , in which the metal appears also to be quadrivalent.

Chlorides.—Iridium appears to form three chlorides, but only two of them — namely, the trichloride and tetrachloride — have been obtained in definite form.

The *dichloride*, $Ir''Cl_2$, is not known in the separate state, but appears to exist in certain double salts, called *hypochloriridites*.

The *trichloride* or *Iridious chloride*, Ir_2Cl_6, is prepared by strongly heating iridium with nitre, adding water and enough nitric acid to saturate the alkali, warming the mixture, and then dissolving the precipitated hydrate of the sesquioxide in hydrochloric acid; it forms a dark yellowish-brown solution. This substance combines with other metallic chlorides, forming compounds called *iridoso-chlorides* or *chloriridites*, which may be prepared by reducing the corresponding chloriridiates with sulphurous acid, hydrogen sulphide, or potassium ferrocyanide. Claus has obtained the compounds $Ir_2Cl_6.6NH_4Cl\ 6OH_2$, $Ir_2Cl_6.6KCl.6OH_2$, and $Ir_2Cl_6.6NaCl.24OH_6$. They are olive-green pulverulent salts, soluble in water.

The *tetrachloride*, or *Iridic chloride*, $IrCl_4$, is obtained in solution by dissolving very finely divided iridium, or one of its oxides, or the trichloride, in nitromuriatic acid, and heating the liquid to the boiling point. On evaporating the solution, it remains in the form of a black, deliquescent, amorphous mass, translucent with dark-red color at the edges; soluble, with reddish-yellow color, in water. It unites with alkaline chlorides, forming compounds called *iridiochlorides* or *chloriridiates*, analogous in composition to the chloroplatinates. The *ammonium salt*, $IrCl_4.2NH_4Cl.OH_2$, and the *potassium salt*, $IrCl_4.2KCl$, are formed, as dark-brown crystalline precipitates, on mixing the solutions of the component chlorides. The potassium salt may also be prepared by passing chlorine over a gently ignited and finely divided mixture of iridium with potassium chloride. It is soluble in boiling water, and crystallizes in black octohedrons, yielding a red powder. The *sodium salt*, $IrCl_4.2NaCl.6OH_2$, prepared like the potassium salt, forms easily soluble black tables and prisms, isomorphous with the corresponding platinum salt.

Iodides. — Iridium forms three iodides, IrI_2, Ir_2I_6, and IrI_4, analogous to the chlorides, and yielding similar double salts with the iodides of the alkali-metals.†

Oxides. — Iridium forms four oxides, IrO, Ir_2O_3, IrO_2, and IrO_3. The *monoxide*, or *hypoiridious oxide*, IrO, is but little known. It is obtained by precipitating an alkaline hypochloriridite with caustic alkali in an atmosphere of carbon dioxide (p. 166); but on exposure to the air it is quickly converted into a higher oxide.

The *sesquioxide*, or *Iridious oxide*, Ir_2O_3, was formerly regarded as the most easily formed and most stable of the oxides of iridium; but, according

* A hexchloride, $IrCl_6$, was said by Berzelius to be obtained in combination with potassium chloride by fusing iridosmine with nitre; but according to Claus, the salt thus formed was really a ruthenium compound, having been prepared by Berzelius from iridosmine containing ruthenium.

† Offler, *Ueber die Iodverbindungen des Iridiums*. Göttingen, 1857.

to Claus, it has a great tendency to take up oxygen and pass to the state of dioxide. It may be prepared by gently igniting a mixture of potassium chloriridite ($Ir_2Cl_6.6KCl$) with sodium carbonate in an atmosphere of carbon dioxide; on treating the product with water, the sesquioxide remains in the form of a black powder insoluble in acids. It forms two hydrates, $Ir_2O_3.3OH_2$, and $Ir_2O_3.5OH_2$. It unites with bases, forming salts which may be called *iridites*. A solution of a chloriridite in excess of lime-water deposits, after standing for some time out of contact of air, a dirty yellow precipitate containing $Ir_2O_3.3CaO$.

The *dioxide*, or *Iridic oxide*, IrO_2, is, according to Claus, the most easily prepared and most stable of all the oxides of iridium, and is always deposited in the form of a bulky, indigo-colored hydrate, $IrO_2.2OH_2$, when a solution of either of the chlorides of iridium or their double salts is boiled with an alkali; but it always retains 3 or 4 per cent. of the alkali. The hydrate may also be obtained by dissolving the hydrated sesquioxide in potash and treating the solution with an acid. It dissolves in acids, forming solutions which are dark-brown when concentrated, reddish-yellow when dilute.

The *trioxide*, or *Periridic oxide*, IrO_3, is not known in the free state, but is formed in combination with potash, when iridium is fused for some time with nitre. The resulting blackish-green mass dissolves in water, forming a deep indigo-colored solution of basic potassium periridiate, leaving a black crystalline powder consisting of acid periridiate.*

Iridium, like the other platinum metals, shows but little tendency to form oxygen-salts. The oxides dissolve in acids, but no definite salts are obtained in this way. The solution of iridic oxide in sulphuric acid has a dark-brown color, which is not modified by potash in the same manner as that of the dichloride, neither does it yield any blue precipitate on boiling.

The only definite oxygen-salts of iridium that have been obtained are double salts containing sulphurous and dithionic acids.

Hypo-iridoso-potassic sulphite, $SO_3Ir''.3SO_3K_2$, is obtained as a white crystalline powder, when the mother-liquor obtained in preparing potassium chloriridite by passing sulphurous oxide through a solution of the chloriridiate, is evaporated to a small bulk.

Sulphides. — Three sulphides of iridium are known, analogous to the first three oxides above described. The *sesquisulphide* and *disulphide* are obtained as brown-black precipitates by treating the solutions of the trichloride and tetrachloride respectively with hydrogen sulphide. The *monosulphide* is a grayish-black substance obtained by decomposing either of the higher sulphides in a close vessel.

Ammoniacal Compounds of Iridium. — The *ammonio-chlorides*, $N_2H_6Ir''Cl_2$ and $N_4H_{12}IrCl_2$, or $[N_2H_4Ir''(NH_4)_2]Cl_2$, together with the corresponding sulphates, are prepared like the platinous compounds of analogous composition, which they also resemble in their properties. The *nitratochloride*, $[N_2H_4Ir''(NH_4)_2](NO_3)Cl$, analogous to Gros' platinum nitrate, is formed by heating the chloride, $N_2H_6IrCl_2$, with strong nitric acid. *Tetrammonio-iridic chloride*, $(N_4H_{12}Ir^{iv})Cl_2$, is obtained as a violet precipitate by treating the nitrate just mentioned with hydrochloric acid.†

The compound, $10NH_3.Ir_2Cl_6$, or $[N_3H_7Ir'''(NH_4)_2]'''_2Cl_6$, to which there is no analogue in the platinum series, is obtained as a flesh-colored crystalline powder by prolonged digestion of ammonium chloriridite with warm aqueous ammonia. The corresponding carbonate, nitrate, and sulphate have also been prepared.‡

* Claus, Ann. Ch. Pharm. lix. 249.
† Skoblikoff, Ann. Ch. Pharm. lxxxiv. 275.
‡ Claus, *Beiträge zur Chemie der Platinmetalle.* Dorpat, 1854.

Iridic solutions (containing the dioxide or tetrachloride) are of a dark brown-red color; iridious solutions (containing the sesquioxide or trichloride) have an olive-green color. The characters of an iridic solution are best observed with sodium chloriridiate, all the other iridic compounds being but slightly soluble.

Iridic solutions give with *ammonium* or *potassium chloride* a crystalline precipitate of ammonium or potassium chloriridiate, which is distinguished from the corresponding platinum precipitate by its dark brown-red color, and further by its reduction to soluble chloriridite when treated with solution of hydrogen sulphide. This reaction serves for the separation of iridium from platinum.

RUTHENIUM.

Atomic weight, 104. Symbol, Ru.

This metal, discovered by Claus, in 1846, occurs in platinum ore, and chiefly in osmiridium, of which there are two varieties — one scaly, consisting almost wholly of osmium, iridium, and ruthenium, while the other, which is granular, contains but mere traces of osmium and ruthenium, but is very rich in iridium and rhodium. To obtain ruthenium, scaly osmiridium is heated to bright redness in a porcelain tube, through which a current of air (freed from carbonic acid by passing through potash, and from organic matter by passing through oil of vitriol) is drawn by means of an aspirator. The osmium and ruthenium are thereby oxidized, the former being carried forward as tetroxide and condensed in caustic potash solution, while the ruthenium oxide remains behind, together with iridium; and by fusing this residue with potassium hydrate, treating the mass with water, and leaving the liquid in a corked bottle for about two hours to clarify, an orange-colored solution of potassium rutheniate is obtained, which, when neutralized with nitric acid, deposits velvet-black ruthenium sesquioxide, and this when washed, dried, and ignited in hydrogen, yields the metal.

Ruthenium thus prepared, forms porous lumps very much like iridium, and is moderately easy to pulverize. It is the most refractory of all metals except osmium. Deville and Debray have, however, fused it by placing it in the hottest part of the oxy-hydrogen flame. After fusion it has a density of 11·4; that of the porous metal is 8·6.

Ruthenium is scarcely attacked by nitromuriatic acid. It is, however, more easily oxidized than platinum, or even than silver. When pure it is easily oxidized by fusion with potassium hydrate, still more easily on addition of a small quantity of nitrate or chlorate, producing potassium rutheniate, which dissolves in water with orange-yellow color.

Chlorides. — Ruthenium is a tetrad, like the other platinum metals, and forms three chlorides, $RuCl_2$, Ru_2Cl_6, and $RuCl_4$.

The *dichloride*, $RuCl_2$, is produced, together with the trichloride, by igniting pulverized ruthenium in a stream of chlorine, the trichloride then volatilizing, while the dichloride remains in the form of a black crystalline powder, insoluble in water and in all acids, even nitro-muriatic acid, and only partially decomposed by alkalies. A soluble dichloride is formed by passing sulphydric acid gas into a solution of the trichloride, a brown sulphide being then precipitated, and the solution acquiring a fine blue color.

The *trichloride* or *Ruthenious chloride*, Ru_2Cl_6, prepared by precipitating a solution of potassic rutheniate with an acid, dissolving the precipitated black oxide in hydrochloric acid, and evaporating, is a yellow-brown, crystalline, very deliquescent mass, becoming dark-green and blue at certain

points when strongly heated. It dissolves easily in water and in alcohol, leaving a small quantity of a yellow insoluble salt.

The concentrated solution of ruthenious chloride, mixed with concentrated solutions of the chlorides of potassium and ammonium, yields the double salts, $Ru_2Cl_6.4KCl$, and $Ru_2Cl_6.4NH_4Cl$, in the form of crystalline precipitates, with violet iridescence, very slightly soluble in water, insoluble in alcohol.

The *tetrachloride* or *Ruthenic chloride*, $RuCl_4$, is known only in its double salts. The *potassium-salt*, $RuCl_4.2KCl$, is prepared by mixing a solution of ruthenic hydrate in hydrochloric acid with potassium chloride, and evaporating to the crystallizing point. It is brown, with rose-colored iridescence, very soluble in water, but insoluble in alcohol. The *ammonium salt*, $RuCl_4.2NH_4Cl$, is prepared like the potassium salt, which it resembles closely.

Oxides. — Ruthenium forms five oxides, viz., RuO, Ru_2O_3, RuO_2, RuO_3, and RuO_4, the fourth, however, being known only in combination.

The *monoxide*, RuO, obtained by calcining the dichloride with sodium carbonate in a current of carbon dioxide, and washing the residue with water, has a dark-gray color and metallic lustre; is not acted upon by acids; but is reduced by hydrogen at ordinary temperatures. — The *sesquioxide*, or *Ruthenious oxide*, Ru_2O_3, is a bluish-black powder, formed by heating the metal in the air. The corresponding hydrate, $Ru_2O_3.3OH$, or RuH_3O_3, is obtained by precipitating ruthenious chloride with an alkaline carbonate, as a blackish-brown substance which dissolves with yellow color in acids. — The *dioxide*, or *Ruthenic oxide*, RuO_2, is a black-blue powder, obtained by roasting the disulphide. *Ruthenic hydrate*, $RuO_2.2OH_2$, or $Ru^{iv}H_4O_4$, is obtained as a gelatinous precipitate by decomposing potassium chlororutheniate with sodium carbonate. — The *trioxide*, RuO_3, commonly called *ruthenic acid*, is known only as a potassium-salt, which is obtained by igniting ruthenium with caustic potash and nitre: it forms an orange-yellow solution. — The *tetroxide*, RuO_4, is a volatile compound, analogous to osmic tetroxide, obtained by heating ruthenium with potash and nitre, in a silver crucible, dissolving the fused mass in water, and passing chlorine through the solution in a tubulated retort, connected by a condensing-tube with a receiver containing potash. The tetroxide then passes over and condenses in the neck of the retort, and in the tube, as a golden-yellow crystalline crust, which melts between 50° and 60°. It is heavier than oil of vitriol, dissolves slightly in water, readily in hydrochloric acid, forming a solution easily decomposed by alcohol, sulphurous acid, and other reducing agents.

Sulphides. — Hydrogen sulphide, passed into a solution of either of the chlorides of ruthenium, usually forms a precipitate consisting of ruthenium sulphide and oxysulphide mixed with free sulphur. The blue solution of the dichloride yields a dark-brown sesquisulphide, Ru_2S_3. When hydrogen sulphide is passed for a long time into a solution of the trichloride, ruthenium disulphide, RuS_2, is formed, as a brown-yellow precipitate, becoming dark-brown by calcination.

Ammoniacal Ruthenium Compounds. — *Tetrammonio-hyporuthenious chloride*, $4NH_3.RuCl_2.3OH_2$, or $[N_2H_4Ru''(NH_4)_2]Cl_2\ 3OH_2$, is formed by boiling the solution of ammonium chlororutheniate ($RuCl_4.2NH_4Cl$), with ammonia. It forms golden-yellow oblique rhombic crystals, very soluble in water, insoluble in alcohol. Treated with silver oxide, it yields the corresponding oxide, $4NH_3.RuO$, which, however, is decomposed by evaporation of its solution, giving off half its ammonia, and leaving the compound $2NH_3.RuO$, or $(N_2H_6Ru'')O$. The carbonate, nitrate, and sulphate, obtained by treating this last-mentioned oxide with the corresponding silver salts, form yellow crystals.

The compounds of ruthenium may readily be distinguished from those of the other platinum-metals, by fusing a few milligrammes of the substance in a platinum-spoon, with a large excess of nitre, leaving it to cool when it ceases to froth, and dissolving the cooled mass in a little distilled water. An orange-yellow solution of potassium rutheniate is thus formed, which on addition of a drop or two of nitric acid, yields a bulky, black precipitate; and on adding hydrochloric acid to the liquid, with the precipitate still in it, and heating it in a porcelain crucible, the oxide dissolves, forming a solution which has a fine orange-yellow when concentrated, and when treated with *hydrogen-sulphide*, till it becomes nearly black, yields a filtrate of a splendid sky-blue color. Characteristic reactions are also obtained with *potassium sulphocyanate*, which colors the liquid deep red, changing to violet on heating, and with *lead acetate*, which forms a purple-red precipitate.

OSMIUM.

Atomic weight, 199. Symbol, Os.

The separation of this metal from iridium, ruthenium, and the other metals with which it is associated in native osmiridium, and in platinum residues, depends chiefly on its ready oxidation with nitric or nitromuratic acid, or by ignition in air or oxygen, and the volatility of the oxide thus produced.

To prepare metallic osmium, the solution obtained by condensing the vapor of osmium tetroxide in potash (p. 385) is mixed with excess of hydrochloric acid, and digested with mercury in a well-closed bottle at 40° C. (104° F.) The osmium is then reduced by the mercury, and an amalgam is formed, which, when distilled in a stream of hydrogen till all the mercury and calomel are expelled, leaves metallic osmium in the form of a black powder (Berzelius). The metal may also be obtained by igniting ammonium chloro-osmite with sal-ammoniac.

The properties of osmium vary according to its mode of preparation. In the pulverulent state it is black, destitute of metallic lustre, which, however, it acquires by burnishing; in the compact state, as obtained by Berzelius's method above described, it exhibits metallic lustre, and has a density of 10. Deville and Debray, by igniting precipitated osmium sulphide in a crucible of gas-coke, at the melting heat of nickel, obtained it in bluish-black, easily divisible lumps. When heated to the melting point of rhodium, it becomes more compact, and acquires a density of 21·3 to 21·4. At a still higher temperature, capable of melting ruthenium and iridium, and volatilizing platinum, osmium likewise volatilizes, but still does not melt; in fact, it is the most refractory of all metals.

Osmium in the finely divided state is highly combustible, continuing to burn when set on fire, till it is all volatilized as tetroxide. In this state also it is easily oxidized by nitric or nitromuriatic acid, being converted into tetroxide. But after exposure to a red heat, it becomes less combustible, and is not oxidized by nitric or nitromuriatic acid. Osmium which has been heated to the melting-point of rhodium, does not give off any vapor of tetroxide when heated in the air to the melting-point of zinc, but takes fire at higher temperatures.

Osmium Chlorides. — Osmium forms three chlorides, analogous to those of iridium and ruthenium. When it is heated in dry chlorine gas, there is formed, first a blue-black sublimate of the dichloride, then a red sublimate of the tetrachloride. The *dichloride*, or *hypo-osmious chloride*, dissolves

in water with dark violet-blue color. It is likewise formed by the action of reducing agents on either of the higher chlorides, into which, on the other hand, it is easily converted by oxidation. The addition of potassium chloride renders it more stable, by forming a double salt. The *trichloride*, Os_2Cl_6, has not been isolated, but is contained in the solution obtained by treating the sesquioxide with hydrochloric acid. It forms double salts with alkaline chlorides. The *potassium-salt*, $Os_2Cl_6.6KCl.6OH_2$, is produced together with potassium chlorosmate, when a mixture of pulverized osmium and potassium chloride is ignited in chlorine gas; it forms dark red-brown crystals.

The *tetrachloride*, or *Osmic chloride*, $OsCl_4$, is the red compound which constitutes the principal part of the product obtained by igniting osmium in chlorine gas. It dissolves with yellow color in water and alcohol, and is decomposed quickly in dilute solution, more slowly in presence of hydrochloric acid or metallic chlorides, yielding a black precipitate of osmic oxide, and a solution of osmium tetroxide in hydrochloric acid.

Osmic chloride unites with the chlorides of the alkali-metals, forming salts sometimes called *osmiochlorides*, or *chlorosmates*. From the solutions of these salts, *hydrogen sulphide*, and *ammonium sulphide*, slowly precipitate a yellow-brown sulphide insoluble in alkaline sulphides; *silver nitrate* forms an olive-green, *stannous chloride* a brown precipitate. *Tannic acid*, on heating, produces a blue color, but no precipitate; *potassium ferrocyanide*, first a green, then a blue color; *potassium iodide*, a deep purple-red color. *Potash* gives a black, *ammonia* a brown precipitate, slowly in the cold, immediately on boiling. Metallic *zinc* and *sodium formate* throw down metallic osmium.

Sodium osmiochloride, $OsCl_4.2NaCl$, prepared by heating a mixture of osmium sulphide and sodium chloride in a current of chlorine, crystallizes in orange-colored rhombic prisms, an inch long, easily soluble in water, and in alcohol. The *potassium* and *ammonium salts*, of analogous composition, are obtained as red-brown crystalline precipitates on adding sal-ammoniac or potassium chloride to the solution of the sodium salt.

Oxides. — Osmium forms five oxides analogous to those of ruthenium. The *monoxide* or *hypo-osmious oxide*, OsO, is obtained by igniting hypo-osmious sulphite in a stream of carbonic acid gas; also as blue-black hydrate, by heating the same salt with strong potash solution in a closed vessel. *Hypo-osmious sulphite*, SO_3Os'' or SO_2,OsO, is a black-blue salt, produced by mixing the aqueous solution of osmium tetroxide with sulphurous acid. — The *sesquioxide* or *osmious oxide*, Os_2O_3, is obtained by heating either of the double salts of the trichloride with sodium carbonate in a stream of carbonic acid gas. It is a black powder insoluble in acids. The *hydrate*, obtained by precipitation, has a dirty brown-red color, is soluble in acids, but does not yield pure salts.

The *dioxide*, or *Osmic oxide*, OsO_2, is obtained as a black insoluble powder, by heating potassium osmiochloride with sodium carbonate in a stream of carbonic acid gas, or in copper-red metallic-shining lumps, by heating the corresponding hydrate. *Osmic hydrate*, $OsO_2.2OH_2$, is obtained by precipitating a solution of potassium osmio-chloride with potash, at the boiling heat, or in greater purity by mixing a solution of potassic osmite, $OsO_3.K_2O$, with dilute nitric acid.

The *trioxide*, OsO_3, is not known in the free state, but combines with alkalies, forming salts called *osmites*, which are produced by the action of reducing agents on the tetroxide in presence of alkalies. The *potassium salt*, $OsO_3.K_2O.2OH_2$, is a rose-colored crystalline powder.

The *tetroxide*, OsO_4, commonly called *osmic acid*, is the volatile, strong-smelling compound, formed when osmium or either of its lower oxides is heated in the air, or treated with nitric or nitromuriatic acid. It may be

prepared by heating osmium in a current of oxygen gas, and condenses in the cool part of the apparatus in colorless, transparent crystals. It melts below 100°, and boils at a temperature a little above its melting point. Its vapor has an intolerably pungent odor; attacks the eyes strongly and painfully, and is excessively poisonous. Osmium tetroxide is dissolved slowly, but in considerable quantity, by water, forming an acid solution. It is a powerful oxidizing agent, decolorizing indigo solution, separating iodine from potassium iodide, converting alcohol into aldehyde and acetic acid, &c. It dissolves in alkalies, forming yellow-red solutions, which are inodorous when cold, but when heated, give off the tetroxide and free oxygen, leaving a residue of alkaline osmite.

Sulphides. — Osmium burns in sulphur-vapor. Five sulphides of osmium are said to exist, analogous to the oxides, the first four being produced by decomposing the corresponding chlorides with hydrogen sulphide, and the tetrasulphide by passing that gas into a solution of the tetroxide. The last is a sulphur-acid, perfectly soluble in water, whereas the others are sulphur-bases, slightly soluble in water, and forming deep yellow solutions.

Ammoniacal Osmium Compounds. — A cold solution of potassium osmite, mixed with sal-ammoniac, yields a yellow crystalline precipitate, consisting, according to Claus, of *hydrated osmammonium chloride*, $(N_2H_6Os'')Cl_2$. An aqueous solution of the tetroxide treated with ammonia, yields a brown-black powder, consisting of $N_2H_8OsO_3$, or $[N_2H_6(OsO)'']O.OH_2$.

Osmiamic Acid, $Os_2N_2O_5H_2$. — The potassium-salt, of this bibasic acid, $Os_2N_2O_5K_2$, is produced by the action of ammonia on a hot solution of osmium tetroxide in excess of potash:

$$6OsO_4 + 8NH_3 + 6OKH = 3Os_2N_2O_5K_2 + 15OH_2 + N_2.$$

It separates as a yellow crystalline powder, and its solution, treated with silver nitrate, yields a precipitate of silver osmiamate, $Os_2N_2O_5Ag_2$, from which the aqueous acid may be prepared by decomposition with hydrochloric acid. It is a strong acid, decomposing, not only the carbonates, but also the chlorides, of potassium and sodium. The osmiamates of the alkali-metals and alkaline earth-metals are soluble in water; the lead, mercury, and silver salts are insoluble.

All osmium compounds, when heated with excess of nitric acid, give off the unpleasant odor of osmium-tetroxide. By ignition in hydrogen gas, they are reduced to metallic osmium, which, as well as the lower oxides, emits the same odor when heated in contact with the air. The reactions of osmium salts in solution have already been described.

GROUP II.

TIN.

Atomic weight, 118. Symbol, Sn. (Stannum.)

This valuable metal occurs in the state of oxide, and more rarely as sulphide: the principal tin mines are those of Saxony and Bohemia, Malacca, and more especially Cornwall. In Cornwall the tin-stone is found as a constituent of metal-bearing veins, associated with copper ore, in granite and slate-rocks; and as an alluvial deposit, mixed with rounded pebbles, in the beds of several small rivers. The first variety is called *mine-* and the

second *stream-tin.* Tin oxide is also found disseminated through the rock itself in small crystals.

To prepare the ore for reduction, it is stamped to powder, washed, to separate as much as possible of the earthy matter, and roasted, to expel sulphur and arsenic: it is then strongly heated with coal, and the metal thus obtained is cast into large blocks. Two varieties of commercial tin are known, called *grain-* and *bar-tin;* the first is the best; it is prepared from the stream ore.

Pure tin has a white color, approaching that of silver; it is soft and malleable, and when bent or twisted emits a peculiar crackling sound; it has a density of 7·3 and melts at 237° C. (457° F.) Tin is but little acted upon by air and water, even conjointly; when heated above its melting point, it oxidizes rapidly, becoming converted into a whitish powder, used in the arts for polishing under the name of *putty-powder.* The metal is attacked and dissolved by hydrochloric acid, with evolution of hydrogen; nitric acid acts with great energy, converting it into a white hydrate of the dioxide.

Tin is a tetrad metal, and forms two well-defined classes of compounds, namely, the *stannous compounds,* in which it is bivalent, as $Sn''Cl_2$, $Sn''I_2$, $Sn''O$, &c., and the *stannic compounds,* in which it is quadrivalent, as $Sn^{iv}Cl_4$, $Sn^{iv}O_2$, &c.; also a few compounds called *stannoso-stannic compounds,* of intermediate composition, and probably formed by combination of stannous and stannic compounds, *e. g.*, $Sn_2Cl_6 = SnCl_2.SnCl_4$; $Sn_2O_3 = SnO.SnO_2$.

Chlorides.—The *dichloride,* or *Stannous chloride,* $SnCl_2$, is obtained in the anhydrous state by distilling a mixture of calomel and powdered tin, prepared by agitating the melted metal in a wooden box until it solidifies. It is a gray, resinous-looking substance, fusible below redness, and volatile at a high temperature.

The *hydrated chloride,* commonly called *tin-salt,* is easily prepared by dissolving metallic tin in hot hydrochloric acid. It crystallizes in needles containing $SnCl_2.2OH_2$, which are freely soluble in a small quantity of water, but are apt to be decomposed in part when put into a large mass, unless hydrochloric acid in excess be present. Solution of stannous chloride is employed as a deoxidizing agent; it reduces the salts of mercury and other metals of the same class. It is also extensively employed as a mordant in dyeing and calico-printing; sometimes also as an antichlore.

Stannous chloride unites with the chlorides of the alkali-metals, forming crystallizable double salts, $SnCl_2.2KCl$, &c., called *Stannoso-chlorides* or *Chlorostannites.*

The *tetrachloride,* or *Stannic chloride,* $SnCl_4$, is an old and very curious compound, formerly called *fuming liquor of Libavius.* It is made by exposing metallic tin to the action of chlorine, or, more conveniently, by distilling a mixture of 1 part of powdered tin with 5 parts of corrosive sublimate It is a thin, colorless, mobile liquid, boiling at 120° C. (248° F.), and yielding a colorless invisible vapor. It fumes in the air, and when mixed with a third part of water, solidifies to a soft fusible mass called *butter of tin.* The solution of stannic chloride is much employed by the dyer for the brightening and fixing of red colors, and is sometimes designated by the old names, "composition, physic, or tin solution;" it is commonly prepared by dissolving metallic tin in a mixture of hydrochloric and nitric acids, care being taken to avoid too great elevation of temperature. The solution when evaporated yields a deliquescent crystalline hydrate, $SnCl_4.5OH_2$.

Stannic chloride forms, with the chlorides of the alkali-metals and alkaline earth-metals, crystalline double salts, called *Stannochlorides* or *Chlorostannates, e. g.*, $SnCl_4.2NH_4Cl$; $SnCl_4.BaCl_2$, &c. It also forms crystalline compounds with the pentachloride and oxychloride of phosphorus, viz., $SnCl_4.PCl_5$, and $SnCl_4.POCl_3$, and a solid compound with phosphine, containing $3SnCl_4.2PH_3$.

The *trichloride*, or *Stannoso-stannic chloride*, known only in solution, is produced by dissolving the sesquioxide in hydrochloric acid. The solution acts like a mixture of the dichloride and tetrachloride.

Fluorides.—*Stannous fluoride*, SnF_2, obtained by evaporating the solution of stannous oxide in hydrofluoric acid, crystallizes in small shining opaque prisms. *Stannic fluoride*, SnF_4, is not known in the free state, but unites with other metallic fluorides, forming crystalline compounds called *stannofluorides* or *fluostannates*, isomorphous with the corresponding silicofluorides, titanofluorides, and zircofluorides. The potassium salt contains $SnF_4.2KCl.OH_2$, the barium salt, $SnF_4.BaF_2$, &c.

Oxides.—The *monoxide*, or *Stannous oxide*, SnO, is produced by heating stannous oxalate out of contact with the air; also by igniting stannous hydrate. This *hydrate*, $2SnO.OH_2$, or $Sn_2H_2O_3$, is obtained as a white precipitate by decomposing stannous chloride with an alkaline carbonate, carbon dioxide gas being at the same time evolved. This hydrate, carefully washed, dried, and heated in an atmosphere of carbon dioxide, leaves anhydrous stannous oxide as a dense black powder, which is permanent in the air, but when touched with a red-hot body, takes fire and burns like tinder, producing the dioxide. The hydrate is freely soluble in caustic potash; the solution decomposes by keeping into metallic tin and dioxide. It dissolves also in sulphuric acid, forming *stannous sulphate*, SO_4Sn'', which crystallizes in needles.

The *sesquioxide*, Sn_2O_3, is produced by the action of hydrated ferric oxide upon stannous chloride: it is a grayish, slimy substance, soluble in hydrochloric acid, and in ammonia. This oxide has been but little examined.

The *dioxide*, or *Stannic oxide*, SnO_2, occurs native as tin-stone or cassiterite, the common ore of tin, and is easily formed by heating tin, stannous oxide, or stannous hydrate in contact with the air. As thus prepared, it is a white or yellowish amorphous powder; but by passing the vapor of stannic chloride mixed with aqueous vapor through a red-hot porcelain tube, it may be obtained in crystals. It is not attacked by acids, even in the concentrated state.

Stannic oxide forms two hydrates, differing from one another in composition and properties; both, however, being acids, and capable of forming salts by exchanging their hydrogen for metals. These hydrates or acids are *stannic acid*, $SnO_2.OH_2$, or SnO_3H_2, and *metastannicacid*, $Sn_5O_{10}.5OH_2$, or $Sn_5O_{15}H_{10}$, the former being capable of exchanging the whole of its hydrogen for metal, and forming the *stannates*, containing SnO_3M_2; while the latter exchanges only one fifth of its hydrogen, forming the *metastannates*, $Sn_5O_{15}H_8M_2$.

Stannic acid is precipitated by acids from solutions of alkaline stannates, also from solution of stannic chloride, by calcium or barium carbonate not in excess; alkaline carbonates throw down an acid stannate. When dried in the air at ordinary temperatures, it has, according to Weber, the composition, $SnO_2.2OH_2$; in a vacuum half the water is given off, leaving $SnO_2.OH_2$.

Stannic hydrate dissolves in the stronger acids, forming the stannic salts; thus with sulphuric acid it forms *stannic sulphate* $(SO_4)_2Sn^{IV}$, or $2SO_3.SnO_2$. *Hydrochloric acid* converts it into the tetrachloride. The stannic salts of oxygen acids are very unstable.

Stannates.—Stannic hydrate exhibits acid much more decidedly than basic properties. It forms easily soluble salts with the alkalies, and from these the insoluble stannates of the earth-metals and heavy metals may be obtained by precipitation. *Sodium stannate*, SnO_3Na_2, which is much used in calico-printing as a "preparing salt" or mordant, is produced on the large scale by fusing tin-stone with hydrate, nitrate, chloride, or sulphide

of sodium; by boiling the tin ore with caustic soda solution; by fusing metallic tin with a mixture of sodium nitrate and carbonate; or heating it with soda solution mixed with sodium nitrate and chloride.*

Metastannic acid is produced by the action of nitric acid upon tin. When dried in the air at ordinary temperatures, it contains $5SnO_2.10OH_2$, or $Sn_5O_{10}H_{15}.5OH_2$, but at 100° it gives off 5 molecules of water, and is reduced to $Sn_5O_{15}H_{10}$. It is a white crystalline powder, insoluble in water and in acids. It dissolves slowly in alkalies forming metastannates, but is gradually deposited in its original state as the solution absorbs carbonic acid from the air. The *potassium salt*, $Sn_5O_{15}H_8K_2$, or $(SnO_2)_5\left\{\begin{matrix}4OH_2\\OK_2\end{matrix}\right.$, may be precipitated in the solid state by adding pieces of solid potash to a solution of metastannic acid in cold potash. It is gummy, uncrystallizable, and strongly alkaline. The *sodium salt*, $Sn_5O_{15}H_8Na_2$, prepared in like manner, is crystallo-granular, and dissolves slowly, but completely, in water. The metastannates exist only in the hydrated state, being decomposed when deprived of their basic water.

Tin Sulphides. — The *monosulphide*, SnS, is prepared by fusing tin with excess of sulphur, and strongly heating the product. It is a lead-gray, brittle substance, fusible at a red heat, and soluble, with evolution of sulphuretted hydrogen, in hot hydrochloric acid. A *sesquisulphide* may be formed by gently heating the above compound with a third of its weight of sulphur: it is yellowish-gray, and easily decompcsed by heat. The *bisulphide*, SnS_2, or *Mosaic gold*, is prepared by exposing to a low red heat, in a glass flask, a mixture of 12 parts of tin, 6 of mercury, 6 of sal-ammoniac, and 7 of flowers of sulphur. Sal-ammoniac, cinnabar, and stannous chloride sublime, while the bisulphide remains at the bottom of the vessel in the form of brilliant gold-colored scales: it is used as a substitute for gold powder. The same compound is obtained as an amorphous light-yellow powder by passing hydrogen sulphide into a solution of stannic chloride.

Stannous salts give with:

Fixed caustic alkalies: white hydrate, soluble in excess.

Ammonia: carbonates of potassium, sodium, and ammonium . . } white hydrate, nearly insoluble in excess.

Hydrogen sulphide . . } black-brown precipitate of monosulphide, soluble in ammonium sulphide containing excess of sulphur, and reprecipitated by acids as yellow bisulphide.

Ammonium sulphide . }

Stannic salts give with:

Fixed caustic alkalies: white hydrate, soluble in excess.
Ammonia: white hydrate, slightly soluble in excess.
Alkaline carbonates: white hydrate, slightly soluble in excess.
Ammonium carbonate: white hydrate, insoluble.
Hydrogen sulphide: yellow precipitate of bisulphide.
Ammonium sulphide: the same, soluble in excess.

Trichloride of gold, added to a dilute solution of stannous chloride, gives rise to a brownish-purple precipitate, called *purple of Cassius* (p. 371).

The useful applications of tin are very numerous. *Tinned plate* consists of iron superficially alloyed with this metal; *pewter*, of the best kind, is chiefly tin, hardened by the admixture of a little antimony, &c. Cooking-

* Richardson and Watts's Chemical Technology, vol. i. pt. iv. p. 35, and pt. v. p. 342.

vessels of copper are usually tinned in the interior. The use of tin solutions in dyeing and calico-printing has been already mentioned.

TITANIUM.

Atomic weight, 50. Symbol, Ti.

This is one of the rarer metals, and is never found in the metallic state. The most important titanium minerals are *rutile*, *brookite*, and *anatase*, which are different forms of titanic oxide, and the several varieties of titaniferous iron, consisting of ferrous titanate, sometimes alone, but more generally mixed with ferric or ferroso-ferric oxide. Occasionally in the slag adhering to the bottom of blast-furnaces in which iron ore is reduced, small brilliant copper-colored cubes, hard enough to scratch glass, and in the highest degree infusible, are found. This substance, of which a single smelting furnace in the Hartz produced as much as 80 pounds, was formerly believed to be metallic titanium. Recent researches of Wöhler, however, have shown it to be a combination of titanium cyanide with titanium nitride. When these crystals are powdered, mixed with potassium hydrate, and fused, ammonia is evolved, and potassium titanate is formed. Metallic titanium in a finely divided state may be obtained by heating titanium and potassium fluoride with potassium. This element is remarkable for its affinity for nitrogen: when heated in the air, it simultaneously absorbs oxygen and nitrogen.

Titanium is tetradic, like tin, and forms two classes of compounds: the *titanic* compounds, in which it is quadrivalent, *e. g.* $Ti^{iv}Cl_4$, $Ti^{iv}O_2$, and the *titanous* compounds, in which it is apparently trivalent but really also quadrivalent, *e. g.*:

$$Ti_2Cl_6, \text{ or } \begin{matrix} TiCl_3 \\ | \\ TiCl_3. \end{matrix}$$

Chlorides. — *Titanous chloride*, Ti_2Cl_6, is produced by passing the vapor of titanic chloride mixed with hydrogen through a red-hot tube; it forms dark violet scales having a strong lustre. *Titanic chloride*, $TiCl_4$, is prepared by passing chlorine over an ignited mixture of titanic oxide and charcoal. It is a colorless volatile fuming liquid, having a specific gravity of 1·7609 at 0°, vapor density = 6·658, and boiling at 135°. It unites very violently with water, and forms definite compounds with ammonia, ammonium chloride, hydrogen cyanide, cyanogen chloride, phosphine, and sulphur tetrachloride.

Fluorides. — *Titanous fluoride*, Ti_2F_6, is obtained as a violet powder by igniting potassio-titanic fluoride in hydrogen gas, and treating the resulting mass with hot water. *Titanic fluoride*, TiF_4, passes over as a fuming colorless liquid, when titanic oxide is distilled with fluor-spar and fuming sulphuric acid in a platinum apparatus. It unites with hydrofluoric acid and metallic fluorides, forming double salts called *titano-fluorides* or *fluotitannates*, isomorphous with the silicofluorides, zircofluorides, &c., *e. g.*, $TiF_4.2KF$; $TiF_4.CaF_2$.

Oxides. — The *sesquioxide*, or *Titanous oxide*, Ti_2O_3, is obtained by igniting the dioxide in hydrogen, as a black powder, which, when heated in the air to a very high temperature, oxidizes to titanic oxide.

The *dioxide* or *Titanic oxide* occurs native in three different forms, viz., as rutile and anatase, which are dimetric, and brookite, which is trimetric; of these, anatase is the purest, and rutile the most abundant. To obtain

pure titanic oxide, rutile or titaniferous iron ore, reduced to fine powder, is fused with twice its weight of potassium carbonate, and the fused mass is dissolved in dilute hydrofluoric acid, whereupon titano-fluoride of potassium soon begins to separate. From the hot aqueous solution of this salt, ammonia throws down snow-white ammonium titanate, which is easily soluble in hydrochloric acid, and when ignited gives reddish-brown lumps of titanic oxide. This oxide is insoluble in water, and in all acids except strong sulphuric acid. By fusing it with six times its weight of acid potassium sulphate, a clear yellow mass is obtained, which dissolves perfectly in warm water.

Titanic oxide appears to form two hydrates or acids, analogous to stannic and metastannic acids. One of these, called *titanic acid*, is precipitated by ammonia from a solution of titanic chloride, as a white powder which dissolves easily in sulphuric, nitric, and hydrochloric acids, even when these acids are rather dilute; but these dilute solutions, when boiled, deposit *metatitanic hydrate*, as a soft white powder, which, like the anhydrous oxide, is insoluble in all acids except strong sulphuric acid.

The *titanates* have not been much studied; most of them may be represented by the formulæ, $TiO_4M_2 = TiO_2.2M_2O$, and $TiO_3M_2 = TiO_2.M_2O$ (the symbol M denoting a univalent metal). The titanates of calcium and iron occur as natural minerals. The titanates of the alkali-metals are formed by fusing titanic oxide with alkaline hydrates, carbonates, or acid sulphates — some of them also in the wet way. When finely pulverized and levigated, they dissolve in moderately warm, concentrated hydrochloric acid; but the greater part of the dissolved titanic acid is precipitated on boiling the solution with dilute acids. The neutral titanates of the alkali-metals, TiO_3M_2, are insoluble in water, but soluble in acids. The titanates of the earth-metals and heavy metals are insoluble, and may be obtained by precipitation.

In a solution of titanic acid in hydrochloric acid, containing as little free acid as possible, *tincture of galls* produces an orange-colored precipitate; *potassium ferrocyanide*, a dark-brown precipitate. Titanic oxide fused with *borax*, or better, with *microcosmic-salt*, in the inner blowpipe flame, forms a glass which is yellow while hot, but becomes violet on cooling. The delicacy of the reaction is much increased by melting a little metallic zinc in the lead.

GROUP III.

LEAD.

Atomic weight, 207. Symbol, Pb (Plumbum).

This abundant and useful metal is altogether obtained from the native sulphide, or *galena*, no other lead-ore being found in large quantity. The reduction is effected in a reverberatory furnace, into which the crushed lead-ore is introduced and roasted for some time at a dull red heat, by which much of the sulphide becomes changed by oxidation to sulphate. The contents of the furnace are then thoroughly mixed, and the temperature raised, when the sulphate and sulphide react upon each other, producing sulphurous oxide and metallic lead:

$$SO_4Pb + PbS = Pb_2 + 2SO_2.$$

Lead melts at 315·5° C. (600° F.), or a little above, and boils and volatilizes at a white heat. By slow cooling it may be obtained in octohedral crystals. In moist air this metal becomes coated with a film of gray matter, thought

to be suboxide, and when exposed to the atmosphere in the melted state it rapidly absorbs oxygen. Dilute acids, with the exception of nitric acid, act but slowly upon lead.

Lead is a tetrad, as shown by the constitution of plumbic ethide, $Pb^{iv}(C_2H_5)_4$; but in its inorganic combinations it appears dyadic, forming but one chloride, $Pb''Cl_2$, with corresponding bromide and iodide. The oxide corresponding to these is $Pb''O$, and there are also higher oxides in which the metal may be regarded either as a dyad or as a tetrad: thus the dioxide PbO_2 may be formulated either as

$$O=Pb=O, \text{ or as } \begin{matrix} O \\ | \\ O \end{matrix} \!\!> Pb.$$

Lead Chloride, $PbCl_2$, is prepared by precipitating a solution of lead nitrate or acetate with hydrochloric acid or common salt. It separates as a heavy white crystalline precipitate, which dissolves in about 33 parts of boiling water, and separates again, on cooling, in needle-shaped crystals.

There are several oxychlorides of lead, one of which, $Pb_3Cl_2O_2$, or $PbCl_2.2PbO$, occurs crystallized in right rhombic prisms on the Mendip Hills, thence called *mendipite*. Another, constituting Pattinson's white oxychloride, Pb_2Cl_2O or $PbCl_2.PbO$, is prepared for use as a pigment by grinding galena with strong hydrochloric acid, dissolving the resulting chloride in hot water, and precipitating with lime-water. A third oxychloride, $PbCl_2.7PbO$, called *patent yellow* or *Turner's yellow*, is prepared by heating 1 part of sal-ammoniac with 10 parts of litharge.

Lead Iodide, PbI_2, is precipitated, on mixing lead nitrate or acetate with potassium iodide, as a bright yellow powder, which dissolves in boiling water, and crystallizes therefrom in beautiful yellow iridescent spangles.

Oxides. — The *monoxide*, PbO, called *litharge* or *massicot*, is the product of the direct oxidation of the metal. It is most conveniently prepared by heating the carbonate to dull redness; common *litharge* is impure monoxide which has undergone fusion. Lead oxide has a delicate straw-yellow color, is very heavy, and slightly soluble in water, giving an alkaline liquid. It is soluble in potash, and crystallizes from the solution in rhombic prisms. At a red heat it melts, and tends to crystallize on cooling. In the melted state it attacks and dissolves siliceous matter with astonishing facility, often penetrating an earthen crucible in a few minutes. It is easily reduced when heated with organic substances of any kind containing carbon or hydrogen. It forms a large class of salts, often called *plumbic salts*, which are colorless if the acid itself is not colored.

Triplumbic tetroxide, or *Red lead*, is not of very constant composition, but generally contains Pb_3O_2 or $2PbO.PbO_2$. It is prepared by exposing the monoxide, which has not been fused, for a long time to the air, at a very faint red heat; it is a brilliant red and extremely heavy powder, decomposed, with evolution of oxygen, by a strong heat, and converted into a mixture of monoxide and dioxide by acids. It is used as a cheap substitute for vermilion.

The *dioxide*, PbO_2, often called *puce* or *brown lead-oxide*, is obtained without difficulty by digesting red lead in dilute nitric acid, whereby lead nitrate is dissolved out, and insoluble dioxide left behind in the form of a deep-brown powder. The dioxide is decomposed by a red heat, yielding up one half of its oxygen. Hydrochloric acid converts it into lead chloride, with disengagement of chlorine; hot oil of vitriol forms with it lead sulphate, and liberates oxygen. The dioxide is very useful in separating sulphurous acid from certain gaseous mixtures, lead sulphate being then produced: $PbO_2 + SO_2 = PbSO_4$.

Diplumbic oxide, or *Lead suboxide*, Pb_2O or Pb—O—Pb, is formed when the monoxide is heated to dull redness in a retort; a gray pulverulent substance is then left, which is resolved by acids into monoxide and metal. It absorbs oxygen with great rapidity when heated, and even when simply moistened with water and exposed to the air.

Lead Nitrate, $(NO_3)_2Pb$ or $N_2O_5\,PbO$, may be obtained by dissolving lead carbonate in nitric acid, or by acting directly upon the metal by the same agent with the aid of heat: it is, as already noticed, a by-product in the preparation of the dioxide. It crystallizes in anhydrous octohedrons, which are usually milk-white and opaque. It dissolves in $7\frac{1}{2}$ parts of cold water, and is decomposed by heat, yielding nitrogen tetroxide, oxygen, and lead monoxide, which obstinately retains traces of nitrogen. When a solution of this salt is boiled with an additional quantity of lead oxide, a portion of the latter is dissolved, and a basic nitrate is generated, which may be obtained in crystals. Carbonic acid separates this excess of oxide in the form of a white compound of lead carbonate and lead hydrate.

Neutral and basic compounds of lead oxide with the trioxide and tetroxide of nitrogen, have been described. These last are probably formed by the combination of a nitrite with a nitrate.

Lead Carbonate; White Lead; CO_3Pb'' or CO_2PbO.—This salt is sometimes found beautifully crystallized in long white needles, accompanying other metallic ores. It may be prepared artificially by precipitating in the cold a solution of the nitrate or acetate with an alkaline carbonate: when the lead solution is boiling, the precipitate is a basic salt containing $2CO_3Pb.\,PbH_2O_2$; it is also manufactured to an immense extent by other means for the use of the painter. Pure lead carbonate is a soft, white powder, of great specific gravity, insoluble in water, but easily dissolved by dilute nitric or acetic acid.

Of the many methods put in practice, or proposed, for making white lead, the two following are the most important and interesting: One of these consists in forming a basic nitrate or acetate of lead by boiling finely powdered litharge with the neutral salt. This solution is then brought into contact with carbonic acid gas, whereby all the excess of oxide previously taken up by the neutral salt is at once precipitated as white lead. The solution strained or pressed from the latter is again boiled with litharge, and treated with carbonic acid: these processes are susceptible of indefinite repetition, whereby the little loss of neutral salt left in the precipitates is compensated. The second, and by far the more ancient method, is rather more complex, and at first sight not very intelligible. A great number of earthen jars are prepared, into each of which is poured a few ounces of crude vinegar; a roll of sheet-lead is then introduced in such a manner that it shall neither touch the vinegar nor project above the top of the jar. The vessels are next arranged in a large building, side by side, upon a layer of stable manure, or, still better, spent tan, and closely covered with boards. A second layer of tan is spread upon the top of the latter, and then a second series of pots; these are in turn covered with boards and decomposing bark, and in this manner a pile of many alternations is constructed. After the lapse of a considerable time, the pile is taken down and the sheets of lead are removed and carefully unrolled; they are then found to be in great part converted into carbonate, which merely requires washing and grinding to be fit for use. The nature of this curious process is generally explained by supposing the vapor of vinegar raised by the high temperature of the fermenting matter, merely to act as a carrier between the carbonic acid evolved from the tan, and the lead oxide formed under the influence of the acid vapor, a neutral acetate, a basic acetate, and a carbonate

being produced in succession, and the action gradually travelling from the surface inwards. The quantity of acetic acid used is, in relation to the lead, quite trifling, and cannot directly contribute to the production of the carbonate. A preference is still given to the product of this old mode of manufacture, on account of its superiority of opacity, or *body*, over that obtained by precipitation. Commercial white lead, however prepared, always contains a certain proportion of hydrate. It is sometimes adulterated with barium sulphate.

When clean metallic lead is put into pure water and exposed to the air, a white, crystalline, scaly powder begins to show itself in a few hours, and very rapidly increases in quantity. This substance may consist of lead hydrate, formed by the action of the oxygen dissolved in the water upon the lead. It is slightly soluble, and may be readily detected in the water. In most cases, however, the formation of this deposit is due to the action of the carbonic acid dissolved in the water: it consists of carbonate in combination with hydrate, and is nearly insoluble in water. When common river or spring water is substituted for the pure liquid, this effect is less observable, the little sulphate, almost invariably present, causing the deposition of a very thin but closely adherent film of lead sulphate upon the surface of the metal, which protects it from further action. It is on this account that leaden cisterns are used with impunity, at least in most cases, for holding water: if the latter were quite pure, it would be speedily contaminated with lead, and the cistern would be soon destroyed. Natural water highly charged with carbonic acid cannot, under any circumstances, be kept in lead or passed through leaden pipes with safety, the carbonate, though very insoluble in pure water, being slightly soluble in water containing carbonic acid.

The soluble salts of lead behave with reagents as follows:—

Caustic *potash* and *soda* precipitate a white hydrate freely soluble in excess. Ammonia gives a similar white precipitate, not soluble in excess. The *carbonates of potassium*, *sodium*, and *ammonium*, precipitate lead carbonate, insoluble in excess. *Sulphuric acid* or a *sulphate* causes a white precipitate of lead sulphate insoluble in nitric acid. *Hydrogen sulphide* and *ammonium sulphide* throw down black lead sulphide. Lead is readily detected before the blowpipe by fusing the compound under examination on charcoal with sodium carbonate, when a bead of metal is easily obtained, which is recognized by its chemical as well as physical properties.

An alloy of 2 parts of lead and 1 of tin constitutes *plumbers' solder;* these proportions reversed give a more fusible compound, called *fine solder.* The lead employed in the manufacture of shot is combined with a little arsenic.

GROUP IV.—IRON METALS.

IRON.

Atomic weight, 56. Symbol, Fe (Ferrum).

This is the most important of all metals: there are few substances to which it yields in interest, when it is considered how very intimately the knowledge of its properties and uses is connected with human civilization.

Metallic iron is of exceedingly rare occurrence: it has been found at Canaan, in Connecticut,* forming a vein about two inches thick in mica-slate; but it

* Phillips' Mineralogy, 4th edit. p. 208.

invariably enters into the composition of those extraordinary stones known to fall from the air, called *meteorites*. Isolated masses of soft malleable iron also, of large dimensions, lie loose upon the surface of the earth in South America and elsewhere, and are presumed to have had a similar origin: these latter, in common with the iron of the undoubted meteorites, contain nickel. In an oxidized condition, the presence of iron may be said to be universal: it constitutes a great part of the common coloring matter of rocks and soils; it is contained in plants, and forms an essential component of the blood of the animal body. It is also very common in the state of bisulphide. Pure iron may be prepared, according to Mitscherlich, by introducing into a Hessian crucible 4 parts of fine iron wire cut small, and 1 part of black iron oxide. This is covered with a mixture of white sand, lime, and potassium carbonate, in the proportions used for glass-making, and a cover being closely applied, the crucible is exposed to a very high degree of heat. A button of pure metal is thus obtained, the traces of carbon and silicium present in the wire having been removed by the oxygen of the oxide.

Pure iron has a white color and perfect lustre: it is extremely soft and tough, and has a specific gravity of 7·8. Its crystalline form is probably the cube, to judge from appearances now and then exhibited. In good bar-iron or wire, a distinct fibrous texture may always be observed when the metal has been attacked by rusting or by the application of an acid, and upon the perfection of this fibre much of its strength and value depends. Iron is the most tenacious of all the metals, a wire $\frac{1}{16}$ of an inch in diameter bearing a weight of 60 lbs. It is very difficult of fusion, and before becoming liquid passes through a soft or pasty condition. Pieces of iron pressed or hammered together in this state cohere into a single mass: the operation is termed *welding*, and is usually performed by sprinkling a little sand over the heated metal, which combines with the superficial film of oxide, forming a fusible silicate, which is subsequently forced out from between the pieces of iron by the pressure applied: clean surfaces of metal are thus presented to each other, and union takes place without difficulty.

Iron does not oxidize in dry air at common temperatures: heated to redness, it becomes covered with a scaly coating of black oxide, and at a high white heat burns brilliantly, producing the same substance. In oxygen gas the combustion occurs with still greater ease. The finely divided spongy metal prepared by reducing the red oxide with hydrogen gas takes fire spontaneously in the air. Pure water, free from air and carbonic acid, does not tarnish a surface of polished iron, but the combined agency of free oxygen and moisture speedily leads to the production of rust, which is a hydrate of the sesquioxide. The rusting of iron is wonderfully promoted by the presence of a little acid vapor. At a red heat, iron decomposes water, evolving hydrogen, and passing into the black oxide. Dilute sulphuric and hydrochloric acids dissolve it freely, with separation of hydrogen. Iron is strongly magnetic up to a red heat, when it loses all traces of that remarkable property.

Iron is a tetrad, forming two classes of compounds; namely, the *ferrous compounds*, in which it is bivalent, *e.g.*, $Fe''Cl_2$, $Fe''O$, $Fe''SO_4$, &c., and the *ferric compounds*, in which it is really quadrivalent, though apparently trivalent, *e.g.*, Fe'''_2Cl_6 or $\begin{vmatrix} Fe'''Cl_3 \\ Fe'''Cl_3 \end{vmatrix}$; Fe'''_2O_3; $Fe'''_2(SO_4)_3$, &c.

Chlorides. — The *dichloride*, or *Ferrous chloride*, $FeCl_2$, is formed by transmitting dry hydrochloric acid gas over red-hot metallic iron, or by dissolving iron in hydrochloric acid. The latter solution yields, when duly concentrated, green crystals of the hydrated dichloride $FeCl_2.4OH_2$; they are very soluble and deliquescent, and rapidly oxidize in the air.

The *trichloride*, or *Ferric chloride*, Fe_2Cl_6, is usually prepared by dissolving ferric oxide in hydrochloric acid. The solution, evaporated to a syrupy consistence, deposits red hydrated crystals, which are very soluble in water and alcohol. It forms double salts with potassium chloride and sal-ammoniac. When evaporated to dryness and strongly heated, much of the chloride is decomposed, yielding sesquioxide and hydrochloric acid: the remainder sublimes, and afterwards condenses in the form of small brilliant red crystals, which deliquesce rapidly. Anhydrous ferric chloride is also produced by the action of chlorine upon the heated metal. The solution of ferric chloride is capable of dissolving a large excess of recently precipitated ferric hydrate, by which it acquires a much darker color.

Iodides. — *Ferrous iodide*, FeI_2, is an important medicinal preparation: it is easily made by digesting iodine with water and metallic iron. The solution is pale-green, and yields, on evaporation, crystals resembling those of the chloride, which rapidly oxidize on exposure to air. It is best preserved in solution in contact with excess of iron. — *Ferric iodide*, Fe_2I_6, is yellowish-red and soluble.

Iron Oxides. — Three oxides of iron are known, namely, ferrous oxide, FeO, and ferric oxide, Fe_2O_3, analogous to the chlorides, and an intermidiate oxide, usually called magnetic iron oxide, containing Fe_3O_4, or $FeO.Fe_2O_3$. A trioxide, FeO_3, is supposed to exist in a class of salts called ferrates, but it has not been isolated.

Monoxide or *Ferrous oxide*, FeO. — This is a very powerful base, neutralizing acids, and isomorphous with magnesia, zinc oxide, &c. It is almost unknown in the separate state, from its extreme proneness to absorb oxygen and pass into the sesquioxide. When a ferrous salt is mixed with caustic alkali or ammonia, a bulky whitish precipitate of ferrous hydrate falls, which becomes nearly black when boiled, the water being separated. This hydrate changes very rapidly when exposed to the air, becoming green and ultimately red-brown. The soluble ferrous salts have commonly a delicate pale-green color and a nauseous metallic taste.

Sesquioxide or *Ferric oxide*, Fe_2O_3. — A feeble base, isomorphous with alumina. It occurs native, most beautifully crystallized, as specular iron ore, in the Island of Elba, and elsewhere; also as red and brown *hæmatite*, the latter being a hydrate. It is artificially prepared by precipitating a solution of ferric sulphate or chloride with excess of ammonia, and washing, drying, and igniting the yellowish-brown hydrate thus produced; fixed alkali must not be used in this operation, as a portion is retained by the oxide. In fine powder, this oxide has a full red color, and is used as a pigment, being prepared for the purpose by calcination of ferrous sulphate; the tint varies somewhat with the temperature to which it has been exposed. The oxide is unaltered in the fire, although easily reduced at a high temperature by carbon or hydrogen. It dissolves in acids, with difficulty after strong ignition, forming a series of reddish salts, which have an acid reaction and an astringent taste. Ferric oxide is not acted upon by the magnet.

Triferro-tetroxide, *Ferrosoferric oxide*, $Fe_3O_4 = FeO.Fe_2O_3$, also called black *iron oxide*, *magnetic oxide*, and *loadstone*. — A natural product, one of the most valuable of the iron ores, often found in regular octohedral crystals, which are magnetic. It may be prepared by mixing due proportions of ferrous and ferric salts, precipitating them with excess of alkali, and then boiling the mixed hydrates; the latter then unite to a black sandy substance, consisting of minute crystals of the magnetic oxide. This oxide is the chief product of the oxidation of iron at a high temperature in the air and in aqueous vapor. It is incapable of forming definite salts.

Ferrates. — When a mixture of one part of pure ferric oxide and four

parts of dry nitre is heated to full redness for an hour in a covered crucible, and the resulting brown, porous, deliquescent mass is treated when cold with ice-cold water, a deep amethystine-red solution of potassium ferrate is obtained. The same salt may be more easily prepared by passing chlorine gas through a strong solution of potash in which recently precipitated ferric hydrate is suspended; it is then deposited as a black powder, which may be drained upon a tile. It consists of FeO_4K_2 or $FeO_3.OK_2$. The solution of the salt gradually decomposes, even in the cold, and rapidly when heated, giving off oxygen and depositing sesquioxide. The solution of potassium ferrate gives no precipitate with salts of calcium, magnesium, or strontium, but when mixed with a barium salt, it yields a deep crimson, insoluble, *barium ferrate*, FeO_4Ba, or $FeO_3.BaO$, which is very permanent. Neither the hydrogen salt nor ferric acid, FeO_4H_2, nor the corresponding anhydrous oxide, FeO_3, is known in the separate state.

Ferrous Sulphate, $SO_4Fe''.7OH_2$, $SO_3.FeO.7OH_2$. — This beautiful and important salt, commonly called *green vitriol*, *iron vitriol*, or *copperas*, may be obtained by dissolving iron in dilute sulphuric acid: it is generally prepared, however, and on a very large scale, by contact of air and moisture with common iron pyrites, which, by absorption of oxygen, readily furnishes the substance in question. Heaps of this material are exposed to the air until the decomposition is sufficiently advanced: the salt produced is then dissolved out by water, and the solution made to crystallize. It forms large green crystals, of the composition above stated, which slowly effloresce and oxidize in the air: it is soluble in about twice its weight of cold water. Crystals containing 4 and also 2 molecules of water have been obtained. Ferrous sulphate forms double salts with the sulphates of potassium and ammonium, containing $(SO_4)_2Fe''K_2.6OH_2$, and $(SO_4)_2Fe''(NH_4)_2.6OH_2$, isomorphous with the corresponding magnesium salts.

Ferric Sulphate, $(SO_4)_3Fe'''_2$, or $3SO_3.Fe_2O_3$, is prepared by adding to a solution of the ferrous salt exactly one half as much sulphuric acid as it already contains, raising the liquid to the boiling-point, and then dropping in nitric acid until the solution ceases to blacken by such addition. The red liquid thus obtained furnishes, on evaporation to dryness, a buff-colored amorphous mass, which dissolves very slowly when put into water. With the sulphates of potassium and ammonium, this salt yields compounds having the form and constitution of alums; the potassium salt, for example, has the composition $(SO_4)_2Fe'''K.12OH_2$. The crystals are nearly destitute of color; they are decomposed by water, and sometimes by long keeping in the dry state. These salts are best prepared by exposing to spontaneous evaporation a solution of ferric sulphate to which potassium or ammonium sulphate has been added.

Ferrous Nitrate $(NO_3)_2Fe''$. — When dilute cold nitric acid is made to act to saturation upon iron monosulphide, and the solution is evaporated in a vacuum, pale-green and very soluble crystals of ferrous nitrate are obtained, which are very subject to alteration. *Ferric nitrate* is readily formed by pouring nitric acid, slightly diluted, upon iron: it is a deep-red liquid, apt to deposit an insoluble basic salt, and is used in dyeing.

Ferrous Carbonate, $CO_3.Fe''$ or $CO_2.Fe''O$. — The whitish precipitate obtained by mixing solutions of ferrous salt and alkaline carbonate: it cannot be washed and dried without losing carbonic acid and absorbing oxygen. This substance occurs in nature as *spathose iron ore*, or *iron spar*, associated with variable quantities of calcium and magnesium carbonates; also in the common *clay iron-stone*, from which nearly all the British iron is made. It is often found in mineral waters, being soluble in excess of

carbonic acid: such waters are known by the rusty matter they deposit on exposure to the air. No ferric carbonate is known.

The *phosphates* of iron are all insoluble.

Iron Sulphides. — Several compounds of iron and sulphur are described: of these the two most important are the following. The *monosulphide*, or *ferrous sulphide*, FeS, is a blackish brittle substance, attracted by the magnet, formed by heating together iron and sulphur. It is dissolved by dilute acids, with evolution of sulphuretted hydrogen gas, and is constantly employed for that purpose in the laboratory, being made by projecting into a red-hot crucible a mixture of $2\frac{1}{2}$ parts of sulphur and 4 parts of iron filings or borings of cast-iron, and excluding the air as much as possible. The same substance is formed when a bar of white-hot iron is brought in contact with sulphur. The *bisulphide*, FeS_2, or iron pyrites, is a natural product, occurring in rocks of all ages, and evidently formed in many cases by the gradual deoxidation of ferrous sulphate by organic matter. It has a brass-yellow color, is very hard, not attracted by the magnet, and not acted upon by dilute acids. When it is exposed to heat, sulphur is expelled, and an intermediate sulphide, Fe_3S_4, analogous to the black oxide, is produced. This substance also occurs native, under the name of *magnetic pyrites*. Iron pyrites is the material now chiefly employed for the manufacture of sulphuric acid; for this purpose the mineral is roasted in a current of air, and the sulphurous acid formed is passed into the lead chambers; the residue consists of iron oxide, frequently containing a quantity of copper large enough to render the extraction of that metal remunerative.

Compounds of iron with *phosphorus*, *carbon*, and *silicium* exist, but little is known respecting them in a definite state. The carbonide is contained in cast-iron and in steel, to which it communicates ready fusibility; the silicium compound is also found in cast-iron. Phosphorus is a very hurtful substance in bar iron, as it renders it brittle or *cold-short*.

Reactions of Iron Salts. — *Ferrous salts* are thus distinguished:

Caustic alkalies, and *ammonia*, give nearly white precipitates, insoluble in excess of the reagent, rapidly becoming green, and ultimately brown, by exposure to air. The *carbonates* of *potassium*, *sodium*, and *ammonium* throw down whitish ferrous carbonate, also very subject to change. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down black ferrous sulphide, soluble in dilute acids. *Potassium ferrocyanide* gives a nearly white precipitate, becoming deep-blue on exposure to air.

Ferric salts are thus characterized:

Caustic fixed alkalies and *ammonia*, give foxy-red precipitates of ferric hydrate, insoluble in excess.

The *carbonates* behave in a similar manner, the carbonic acid escaping.

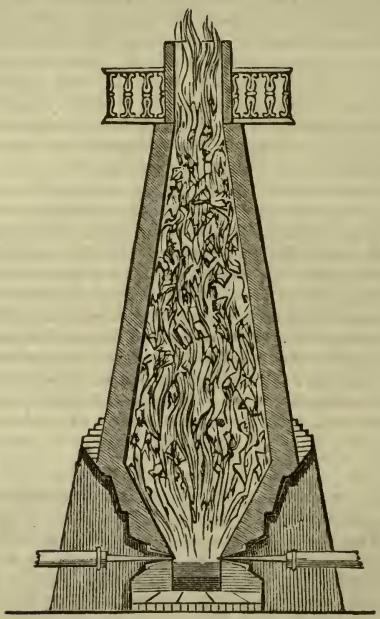
Hydrogen sulphide gives a nearly white precipitate of sulphur, and reduces the sesquioxide to monoxide. *Ammonium sulphide* gives a black precipitate, slightly soluble in excess. *Potassium ferrocyanide* yields Prussian blue. Tincture or infusion of *gall-nuts* strikes intense bluish-black with the most dilute solutions of ferric salts.

Iron Manufacture. — This most important branch of industry consists, as now conducted, of two distinct parts — viz., the production from the ore of a fusible carbonide of iron, and the subsequent decomposition of the carbonide, and its conversion into pure or malleable iron.

The clay-iron ore is found in association with coal, forming thin beds or nodules: it consists, as already mentioned, of ferrous carbonate mixed with

clay; sometimes lime and magnesia are also present. It is broken in pieces, and exposed to heat in a furnace resembling a lime-kiln, by which the water and carbonic acid are expelled, and the ore rendered dark-colored, denser, and also magnetic: it is then ready for reduction. The furnace in which this operation is performed is usually of very large dimensions, 50 feet or more in height, and constructed of brickwork with great solidity, the interior being lined with excellent fire-bricks: the shape will be understood from the section shown in fig. 173. The furnace is close

Fig. 173.



at the bottom, the fire being maintained by a powerful artificial blast introduced by two or tree *twyere-pipes*, as shown in the section. The materials, consisting of due proportions of coke or carbonized coal, roasted ore, and limestone, are constantly supplied from the top, the operation proceeding continuously night and day, often for years, or until the furnace is judged to require repair. In the upper part of the furnace, where the temperature is still very high, and where combustible gases abound, the iron of the ore is probably reduced to the metallic state, being disseminated through the earthy matter of the ore. As the whole sinks down and attains a still higher degree of heat, the iron becomes converted into carbonide by *cementation*, while the silica and alumina unite with the lime, purposely added, to a kind of glass or *slag*, nearly free from iron oxide. The carbonide and slag, both in a melted state, reach at last the bottom of the furnace, where they arrange themselves in the order of their densities: the slag flows out at certain apertures contrived for the purpose, and the iron is discharged from time to time, and suffered to run into rude moulds of sand by opening an orifice at the bottom of the recipient, previously stopped

with clay. Such is the origin of crude or cast-iron, of which there are several varieties, distinguished by differences of color, hardness, and composition, and known by the names of *gray*, *black*, and *white* iron. The first is for most purposes the best, as it admits of being filed and cut with perfect ease. The black and gray kinds probably contain a mechanical admixture of graphite, which separates during solidification.

A great improvement has been made in the above-described process, by substituting raw coal for coke, and blowing hot air instead of cold into the furnace. This is effected by causing the air, on leaving the blowing-machine, to circulate through a system of red-hot iron pipes, until its temperature becomes high enough to melt lead. This alteration has already effected a prodigious saving in fuel, without, it appears, any injury to the quality of the product.

The conversion of cast into bar iron is effected chiefly by an operation called *puddling;* previous to which, however, it commonly undergoes a process called *refining*. It is remelted, in contact with the fuel, in small low furnaces called *refineries*, while air is blown over its surface by means of twyeres. The effect of this operation is to deprive the iron of a great part of the carbon and silicium associated with it. The metal thus purified is run out into a trench, and suddenly cooled, by which it becomes white, crystalline, and exceedingly hard: in this state it is called *fine metal*. The puddling process is conducted in an ordinary reverberatory furnace, into which the charge of fine metal is introduced by a side aperture. This is speedily melted by the flame, and its surface covered with a crust or oxide. The workman then, by the aid of an iron tool, diligently stirs the melted mass, so as intimately to mix the oxide with the metal: he now and then also throws in a little water, with the view of promoting more rapid oxidation. Small jets of blue flame soon appear upon the surface of the iron, and the latter, after a time, begins to lose its fluidity, and acquires, in succession, a pasty and a granular condition. At this point the fire is strongly urged, the sandy particles once more cohere, and the contents of the furnace now admit of being formed into several large balls or masses, which are then withdrawn, and placed under an immense hammer, moved by machinery, by which each becomes quickly fashioned into a rude bar. This is reheated, and passed between grooved cast-iron rollers, and drawn out into a long bar or rod. To make the best iron, the bar is cut into a number of pieces, which are afterwards piled or bound together, again raised to a welding heat, and hammered or rolled into a single bar; and this process of *piling* or *fagoting* is sometimes twice or thrice repeated, the iron becoming greatly improved thereby.

The general nature of the change in the puddling furnace is not difficult to explain. Cast iron consists essentially of iron in combination with carbon and silicium. When strongly heated with iron oxide, those compounds undergo decomposition, the carbon and silicium becoming oxidized at the expense of the oxygen of the oxide. As this change takes place, the metal gradually loses its fusibility, but retains a certain degree of adhesiveness, so that when at last it comes under the tilt-hammer, or between the rollers, the particles of iron become agglutinated into a solid mass, while the readily fusible silicate of the oxide is squeezed out and separated.

All these processes are, in Great Britain, performed with coal or coke; but the iron obtained is, in many respects, inferior to that made in Sweden and Russia from the magnetic oxide, by the use of wood charcoal, — a fuel too dear to be extensively employed in England. Plate iron is, however, sometimes made with charcoal.

Steel. — A very remarkable and most useful substance, prepared by heating iron in contact with charcoal. Bars of Swedish iron are imbedded in charcoal powder, contained in a large rectangular crucible or chest of

some substance capable of resisting the fire, and exposed for many hours to a full red heat. The iron takes up, under these circumstances, from 1·3 to 1·7 per cent. of carbon, becoming harder, and at the same time fusible, with a certain diminution, however, of malleability. The active agent in this cementation process is probably carbonic monoxide: the oxygen of the air in the crucible combines with the carbon to form that substance, which is afterwards decomposed by the heated iron, one half of its carbon being abstracted by the latter. The carbon dioxide thus formed takes up an additional dose of carbon from the charcoal, and again becomes monoxide, the oxygen, or rather the carbon dioxide, acting as a carrier between the charcoal and the metal. The product of this operation is called *blistered* steel, from the blistered and rough appearance of the bars: the texture is afterwards improved and equalized by welding a number of these bars together, and drawing the whole out under a light tilt-hammer.

Some chemists have recently asserted that nitrogen is necessary for the production of steel, and have, in fact, attributed to its presence the peculiar properties of this material; others, again, have disputed this assertion, and believe that the transformation of iron into steel depends upon the assimilation of carbon only; experimentally, the question remains undecided.

Excellent steel is obtained by fusing gray cast-iron with tungstic oxide; the carbon of the iron reduces the tungstic oxide to tungsten (p. 424), which forms with the iron an alloy possessing the properties of steel. The quantity of tungsten thus absorbed by the iron is very small, and some chemists attribute the properties of the so-called tungsten steel to the general treatment rather than to the presence of tungsten.

The most perfect kind of steel is that which has undergone fusion, having been cast into ingot-moulds, and afterwards hammered: of this all fine cutting instruments are made. It is difficult to forge, requiring great skill and care on the part of the operator.

Steel may also be made directly from some particular varieties of cast-iron, as that from spathose iron ore containing a little manganese. The metal is retained, in a melted state, on the hearth of a furnace, while a stream of air plays upon it, and causes partial oxidation: the oxide produced reacts, as before stated, on the carbon of the iron, and withdraws a portion of that element. When a proper degree of stiffness or pastiness is observed in the residual metal, it is withdrawn, and hammered or rolled into bars. The *wootz*, or native steel of India, is probably made in this manner. Annealed cast iron, sometimes called *run-steel*, is now much employed as a substitute for the more costly products of the forge: the articles, when cast, are imbedded in powdered iron ore, or some earthy material, and, after being exposed to a moderate red heat for some time, are allowed to cool slowly, by which a very extraordinay degree of softness and malleability is attained. It is very possible that some little decarbonization may take place during this process.

Bessemer steel is produced by forcing atmospheric air into melted cast-iron. The carbon being oxidized more readily than the iron, it is converted into carbon monoxide, which escapes in a sufficiently heated state to take fire on coming in contact with atmospheric air. Considerable heat is generated by the oxidation of the carbon and iron, so that the temperature is kept above the melting point of steel during the whole of the operation. When the decarburation has been carried far enough, the current of air is stopped, and a small quantity of white pig-iron, containing a large amount of manganese, is dropped into the liquid metal. This serves to facilitate the separation of any gas retained with the melted metal, which, after a few minutes' rest, is run into ingot-moulds.

The most remarkable property of steel is that of becoming exceedingly

hard when quickly cooled. When heated to redness, and suddenly quenched in cold water, steel, in fact, becomes capable of scratching glass with facility: if reheated to redness, and once more left to cool slowly, it again becomes nearly as soft as ordinary iron; and between these two conditions, any required degree of hardness may be attained. The articles, forged into shape, are first hardened in the manner described; they are then *tempered*, or *let down* by exposure to a proper degree of annealing heat, which is often judged of by the color of the thin film of oxide which appears on the polished surface. Thus, a temperature of about 221° C. (430° F.), indicated by a faint straw color, gives the proper temper for razors: that for scissors, penknives, &c., is comprised between 243° C. (470° F.) and 254° C. (490° F.), and is indicated by a full-yellow or brown tint. Swords and watch-springs require to be softer and more elastic, and must be heated to 288° C. (550° F.) or 293° C. (560° F.), or until the surface becomes deep blue. Attention to these colors has now become of less importance, as metal baths are often substituted for the open fire in this operation.

NICKEL.

Atomic weight, 58·8. Symbol, Ni.

Nickel is found in tolerable abundance in some of the metal-bearing veins of the Saxon mountains, in Westphalia, Hessia, Hungary, and Sweden, chiefly as arsenide, the *kupfernickel* of mineralogists, so called from its yellowish-red color. The word *nickel* is a term of detraction, having been applied by the old German miners to what was looked upon as a kind of false copper ore.

The artificial, or perhaps rather merely fused, product, called *speiss*, is nearly the same substance, and may be employed as a source of the nickel-salts. This metal is found in meteoric iron, as already mentioned.

Nickel is easily prepared by exposing the oxalate to a high white heat, in a crucible lined with charcoal, or by reducing one of the oxides by means of hydrogen at a high temperature. It is a white, malleable metal, having a density of 8·8, a high melting-point, and a less degree of oxidability than iron, since it is but little attacked by dilute acids. Nickel is strongly magnetic, but loses this property when heated to 350°.

Nickel, from its resemblance to iron and cobalt, is regarded as a tetrad, although it forms only one chloride, in which it is bivalent, and no oxygen-salts analogous to the ferric salts.

Nickel Chloride, $Ni''Cl_2$.—This compound is easily prepared by dissolving oxide or carbonate of nickel in hydrochloric acid. A green solution is obtained which furnishes crystals of the same color, containing water. When rendered anhydrous by heat, the chloride is yellow, unless it contains cobalt, in which case it has a tint of green.

Nickel Oxides. — Nickel forms two oxides analogous to the two principal oxides of iron.

The *monoxide*, $Ni''O$, is prepared by heating the nitrate to redness, or by precipitating a soluble nickel salt with caustic potash, and washing, drying, and igniting the apple-green hydrated oxide thrown down. It is an ashy-gray powder, freely soluble in acids, which it completely neutralizes, forming salts isomorphous with those of magnesium and the other members of the same group. Nickel salts, when hydrated, have usually a beautiful emerald-green color; in the anhydrous state they are yellow.

The *sesquioxide*, Ni_2O_3, is a black insoluble substance, prepared by passing chlorine through the hydrated monoxide suspended in water; nickel chloride is then formed, and the oxygen of the oxide decomposed is transferred to a second portion. It is also produced when a salt of nickel is mixed with a solution of bleaching-powder. The sesquioxide is decomposed by heat, and evolves chlorine when treated with hot hydrochloric acid.

Nickel Sulphate, $SO_4Ni.7OH_2$.—This is the most important of the nickel-salts. It forms green prismatic crystals, which require 3 parts of cold water for solution. Crystals with 6 molecules of water have also been obtained. It forms with the sulphates of potassium and ammonium beautiful double salts, $(SO_4)_2Ni''K.6OH_2$, and $(SO_4)_2Ni''(NH_4).6OH_2$, isomorphous with the corresponding magnesium salts.

When a strong solution of oxalic acid is mixed with sulphate of nickel, a pale bluish-green precipitate of oxalate falls after some time, very little nickel remaining in solution. The oxalate can thus be obtained for preparing the metal.

Nickel Carbonate, CO_3Ni. — When solutions of nickel sulphate or chloride and of sodium carbonate are mixed, a pale-green precipitate falls, which is a combination of nickel carbonate and hydrate. It is readily decomposed by heat.

Pure nickel-salts are conveniently prepared on the small scale from crude speiss or kupfernickel by the following process: The mineral is broken into small fragments, mixed with from one fourth to half its weight of iron filings, and the whole dissolved in nitromuriatic acid. The solution is gently evaporated to dryness, the residue treated with boiling water, and the insoluble iron arsenate removed by a filter. The liquid is then acidulated with hydrochloric acid, treated with hydrogen sulphide in excess, which precipitates the copper, and, after filtration, boiled with a little nitric acid to bring back the iron to the state of sesquioxide. To the cold and largely diluted liquid solution, acid sodium carbonate is gradually added, by which the ferric oxide may be completely separated without loss of nickel-salt. Lastly, the filtered solution, boiled with sodium carbonate in excess, yields an abundant pale-green precipitate of nickel carbonate, from which all the other compounds may be prepared.

The precipitate thus obtained may still, however, contain cobalt, the separation of which is not very easy. Several methods of separating these metals have been proposed, the best of which is, perhaps, that of H. Rose. The mixed oxides or carbonates being dissolved in excess of hydrochloric acid, the solution, largely diluted with water, is super-saturated with chlorine gas, whereby the cobalt monoxide is converted into sesquioxide, while the nickel monoxide remains unaltered. The liquid is next mixed with excess of recently precipitated barium carbonate, left to stand for twelve to eighteen hours, and shaken up from time to time. The whole of the cobalt is thereby thrown down as sesquioxide, while the nickel remains in solution, and may be precipitated as hydrate by potash, after the barium also contained in the solution has been removed by precipitation with sulphuric acid.*

Nickel-salts are well characterized by their behavior with reagents.

Caustic alkalies give a pale apple-green precipitate of hydrate, insoluble in excess. *Ammonia* affords a similar precipitate, which is soluble in excess, with deep purplish-blue color. *Potassium* and *sodium carbonates* give pale-green precipitates. *Ammonium carbonate*, a similar precipitate, soluble in excess, with blue color. *Potassium ferrocyanide* gives a greenish-white pre-

* For other modes of separating nickel and cobalt, see Gmelin's Handbook, vol. v. pp. 355–360; and Watts's Dictionary of Chemistry, vol. i. p. 1046.

cipitate. *Potassium cyanide* produces a green precipitate, which dissolves in an excess of the precipitant to an amber-colored liquid, and is reprecipitated by an addition of hydrochloric acid. *Hydrogen sulphide* occasions no change, if the nickel be in combination with a strong acid. *Ammonium sulphide* produces a black precipitate of nickel sulphide, which dissolves slightly in excess of the precipitant with dark-brown color. Nickel sulphide when once precipitated is insoluble in dilute hydrochloric acid; it is soluble in nitromuriatic and in hot nitric acid.

The chief use of nickel in the arts is in the preparation of a white alloy, sometimes called German silver, made by melting together 100 parts of copper, 60 of zinc, and 40 of nickel. This alloy is very malleable, and takes a high polish.

COBALT.

Atomic weight, 58·8. Symbol, Co.

This substance bears, in many respects, a close resemblance to nickel: it is often associated with the latter in nature, and may be obtained from its compounds by similar means.

A cobalt-salt free from nickel may be prepared by Rose's process just described. The precipitate, consisting of cobalt sesquioxide mixed with barium carbonate, is boiled with hydrochloric acid to reduce the cobalt sesquioxide to monoxide, and dissolve it as a chloride together with the barium. The latter metal is then precipitated by sulphuric acid, and from the filtered liquid the cobalt may be precipitated as hydrate by potash. A solution of cobalt free from nickel may also be obtained by precipitating the mixed solution with oxalic acid; the whole of the nickel is thereby precipitated, together with a small portion of the cobalt, leaving pure cobalt in solution.

Cobalt is a white, brittle, very tenacious metal, having a specific gravity of 8·5, and a very high melting-point. It is unchanged in the air, and but feebly attacked by dilute hydrochloric and sulphuric acids. It is strongly magnetic.

Cobalt forms two classes of salts, analogous in composition to the ferrous and ferric salts; but the cobaltic salts, in which the metal is apparently trivalent, are very unstable.

Chlorides. — The *dichloride* or *Cobaltous chloride*, $Co''Cl_2$, is easily prepared by dissolving the oxide in hydrochloric acid; or it may be prepared directly from *cobalt-glance*, the native arsenide, by a process exactly similar to that described in the case of nickel. It forms a deep rose-red solution, which, when sufficiently strong, deposits hydrated crystals of the same color: when the liquid is evaporated by heat to a very small bulk, it deposits anhydrous crystals, which are blue: these latter by contact with water again dissolve to a red liquid. A dilute solution of cobalt chloride constitutes the well-known *blue sympathetic ink:* characters written on paper with this liquid are invisible, from their paleness of color, until the salt has been rendered anhydrous by exposure to heat, when the letters appear blue. On laying it aside, moisture is absorbed, and the writing once more disappears. Green sympathetic ink is a mixture of the chlorides of cobalt and nickel.

The *trichloride*, or *Cobaltic chloride*, Co_2Cl_6, is obtained in solution by dissolving the sesquioxide in hydrochloric acid, and in small quantity by saturating a solution of the dichloride with chlorine gas. The liquid has

a dark-brown color, but easily decomposes, giving off chlorine and leaving the rose-colored dichloride.

Oxides.—Cobalt forms two oxides analogous to those of nickel, also two or three of intermediate composition but not very well defined. The *monoxide*, or *Cobaltous oxide*, $Co''O$, is a gray powder, very soluble in acids, and is a strong base, isomorphous with magnesia, affording salts of a fine red tint. It is prepared by precipitating cobaltous sulphate or chloride with sodium carbonate, and washing, drying, and igniting the precipitate. When the cobalt-solution is mixed with caustic potash, a beautiful blue precipitate falls, which, when heated, becomes violet, and at length dirty red, from absorption of oxygen and a change in the state of hydration.

The *sesquioxide*, or *Cobaltic oxide*, Co_2O_3, is a black, insoluble, neutral powder, obtained by mixing solutions of cobalt and chloride of lime. It dissolves in acids, yielding the cobaltic salts.

Cobaltoso-cobaltic oxide, Co_3O_4, analogous to the magnetic oxide of iron, is formed when cobaltous nitrate or oxalate, or hydrated cobaltic oxide, is heated in contact with the air. According to Frémy, it is a salifiable base.

Another oxide, of acid character, is said to be obtained in the form of a potassium salt by fusing the monoxide or sesquioxide with potassium hydrate. A crystalline salt is thus formed consisting, according to Schwarzenberg, of $3Co_3O_5.K_2O.\ 3\,Aq.$

Cobaltous Sulphate, $SO_4Co''.7OH_2$.—This salt forms red crystals, requiring for solution 24 parts of cold water: they are identical in form with those of magnesium sulphate. It combines with the sulphates of potassium and ammonium, forming double salts, which contain, as usual, 6 molecules of water.

A solution of oxalic acid added to cobaltous sulphate occasions, after some time, the separation of nearly the whole of the base in the state of oxalate.

Cobaltous Carbonate.—The alkaline carbonates produce in solutions of cobalt a pale peach-blossom-colored precipitate of combined carbonate and hydrate, containing $3\ CoH_3O_2.2CO_3Co$.

Ammoniacal Cobalt Compounds.—Cobaltous salts treated with ammonia in a vessel protected from the air, unites with the ammonia, forming compounds which may be called *ammonio-cobaltous salts*. Most of them contain 6 molecules of ammonia to 1 molecule of the cobalt salt; thus the chloride contains $CoCl_2.6NH_3.\ Aq.$; the nitrate, $Co(NO_3)_2.6NH_3.\ 2\ Aq.$ They are generally crystallizable and of a rose-color, soluble without decomposition in ammonia, but decomposed by water, with formation of a basic salt. H. Rose, by treating dry cobalt chloride with ammonia-gas, obtained the compound $CoCl_2.4NH_3$; and in like manner an ammonio-sulphate has been formed containing $SO_4Co.6NH_3$.

When an ammoniacal solution of cobalt is exposed to the air, oxygen is absorbed, the liquid turns brown, and new salts are formed containing a higher oxide of cobalt (either Co_2O_3 or CoO_2), and therefore designated generally as *peroxidized ammonio-cobalt salts*. Several of them, containing different bases, are often formed at the same time.

Most of the peroxidized ammonio-cobalt salts are composed of cobaltic salts united with two or more molecules of ammonia. The composition of the normal salts may be illustrated by the chlorides, as in the following table:—

Tetrammonio-cobaltic chloride . .	$Co_2Cl_6\ .\ 4NH_3$
Hexammonio-cobaltic chloride . .	$Co_2Cl_6\ .\ 6NH_3$

Octammonio-cobaltic (or fusco-cobaltic) chloride	$Co_2Cl_6 . 8NH_3$
Decammonio-cobaltic (roseo- and purpureo-cobaltic) chloride . . .	$Co_2Cl_6 . 10NH_3$
Dodecammonio-cobaltic (or luteo-cobaltic) chloride	$Co_2Cl_6 . 12NH_3$.

The formulæ of the corresponding normal nitrates are deduced from the preceding by substituting NO_3 for Cl; those of the sulphates, oxalates, and other bibasic salts, by substituting SO_4, C_2O_4, &c., for Cl_2. Thus *decammonio-cobaltic sulphate* $= Co_2(SO_4)_3.10NH_3$. There are also several acid and basic sats of the same ammonia-molecules. Further, there is a class of salts containing the elements of nitrogen dioxide or nitrosyl, NO, in addition to ammonia, *e. g.*, *decammonio-nitroso-obaltic* or *xantho-cobaltic oxychloride*, $Co_2Cl_4O.10NH_3.N_2O_2$. Lastly, Frémy has obtained ammoniacal compounds (*oxy-cobaltic salts*) containing salts of cobalt corresponding to the dioxide.*

Cobaltous salts have the following characters:

Solution of *potash* gives a blue precipitate, changing by heat to violet and red. *Ammonia* gives a blue precipitate, soluble with difficulty in excess, with brownish-red color. *Sodium carbonate* affords a pink precipitate. *Ammonium carbonate* a similar compound, soluble in excess. *Potassium ferrocyanide* gives a grayish-green precipitate. *Potassium cyanide* affords a yellowish-brown precipitate, which dissolves in an excess of the precipitant. The clear solutions, after boiling, may be mixed with hydrochloric acid without giving a precipitate. *Hydrogen sulphide* produces no change, if the cobalt be in combination with a strong acid. *Ammonium sulphide* throws down black sulphide of cobalt, insoluble in dilute hydrochloric acid.

Cobaltic salts, formed by dissolving cobaltic oxide in acids, give with *potash* a dark-brown precipitate of hydrated cobaltic oxide; with ammonia a brownish-red solution; with the *fixed alkaline carbonates* a green solution, which deposits a small quantity of cobaltic oxide; with *ammonium sulphide* (after saturation of the free acid by ammonia) a black precipitate.

Oxide of cobalt is remarkable for the magnificent blue color it communicates to glass: indeed, this is a character by which its presence may be most easily detected, a very small portion of the substance to be examined being fused with borax on a loop of platinum wire before the blowpipe; the production of this color both in the inner and in the outer flame distinguishes cobalt from all other metals.

The substance called *smalt*, used as a pigment, consists of glass colored by cobalt: it is thus made: — The cobalt ore is roasted until nearly free from arsenic, and then fused with a mixture of potassium carbonate and quartz-sand, free from oxide of iron. Any nickel that may happen to be contained in the ore then subsides to the bottom of the crucible as arsenide: this is the *speiss* of which mention has already been made. The glass, when complete, is removed and poured into cold water: it is afterwards ground to powder and elutriated. *Cobalt-ultramarine* is a fine blue color prepared by mixing 16 parts of freshly-precipitated alumina with 2 parts of cobalt phosphate or arsenate: this mixture is dried and slowly heated to redness. By daylight the color is pure blue, but by artificial light it is violet. A similar compound, of a fine green color, is formed by igniting zinc oxide with cobalt-salts. *Zaffer* is the roasted cobalt ore mixed with siliceous sand,

* For the preparation and properties of all these salts, see Watts's Dictionary of Chemistry, vol. i. p. 1051. Their rational formula are similar to those of the ammoniacal platinum salts (p. 375).

and reduced to fine powder; it is used in enamel painting. A mixture in due proportions of the oxides of cobalt, manganese, and iron is used for giving a fine black color to glass.

MANGANESE.

Atomic weight, 55. Symbol, Mn.

Manganese is tolerably abundant in nature in an oxidized state, forming, or entering into the composition of, several interesting minerals. Traces of this substance are very frequently found in the ashes of plants.

Metallic manganese, or perhaps, strictly, manganese carbonide, may be prepared by the following process: — The carbonate is calcined in an open vessel, by which it becomes converted into a dense brown powder: this is intimately mixed with a little charcoal, and about one-tenth of its weight of anhydrous borax. A charcoal crucible is next prepared by filling a Hessian or Cornish crucible with moist charcoal powder, introduced a little at a time, and rammed as hard as possible. A smooth cavity is then scooped in the centre, into which the above-mentioned mixture is compressed, and covered with charcoal powder. The lid of the crucible is then fixed, and the whole arranged in a very powerful wind-furnace. The heat is slowly raised until the crucible becomes red-hot, after which it is urged to its maximum for an hour or more. When cold, the crucible is broken up, and the metallic button of manganese extracted.

Deville has lately prepared pure manganese by reducing pure manganese oxide with an insufficient quantity of sugar charcoal in a crucible made of caustic lime. Thus prepared, metallic manganese possesses a reddish lustre like bismuth; it is very hard and brittle, and, when powdered, decomposes water, even at the lowest temperature. Dilute sulphuric acid dissolves it with great energy, evolving hydrogen. Brunner produced metallic manganese from manganese and sodium fluoride by means of sodium. The metal obtained by this process scratches glass and hardened steel, and has a specific gravity of 7·13.

Manganese, from its general relations to the metals of the iron group, is usually regarded as a tetrad, forming a dichloride and trichloride analogous to the iron chlorides, together with oxides and other compounds of corresponding constitution. It is also said to form a heptachloride, Mn_2Cl_{14}, or $\left|\begin{matrix}MnCl_7\\MnCl_7\end{matrix}\right|$, according to which it should be regarded as an octad; but the composition of this compound is not very well established.

Manganese Chlorides. — The *dichloride* or *Manganous chloride* may be prepared in a state of purity from the dark-brown liquid residue of the preparation of chlorine from manganese dioxide and hydrochloric acid, which often accumulates in the laboratory to a considerable extent in the course of investigation: from the pure chloride, the carbonate and all other salts can be conveniently obtained. The liquid referred to consists chiefly of the mixed chlorides of manganese and iron; it is filtered, evaporated to perfect dryness, and the residue is slowly heated to dull ignition in an earthen vessel, with constant stirring. The iron chloride is thus either volatilized, or converted by the remaining water into insoluble sesquioxide, while the manganese salt is unaffected. On treating the grayish-looking powder thus obtained with water, the manganese chloride is dissolved out, and may be separated by filtration from the iron oxide. Should a trace of the latter yet remain, it may be got rid of by boiling the liquid for a few

minutes with a little manganese carbonate. The solution of the chloride has usually a delicate pink color, which becomes very manifest when the salt is evaporated to dryness. A strong solution deposits rose-colored tabular crystals, which contain 4 molecules of water; they are very soluble and deliquescent. The chloride is fusible at a red-heat, is decomposed slightly at that temperature by contact with air, and is dissolved by alcohol, with which it forms a crystallizable compound.

The *trichloride*, or *Manganic chloride*, Mn_2Cl_6, is formed when precipitated manganese oxide is immersed in cold dilute hydrochloric acid, the oxide then dissolving quietly without evolution of gas. Heat decomposes the trichloride into the monochloride and free chlorine.

Heptachloride, $Mn_2Cl_{14}(?)$. — When potassium permanganate is dissolved in strong sulphuric acid, and fused sodium chloride is added by small portions at a time, a greenish-yellow gas is given off, which condenses at 0° to a greenish-brown liquid. This compound, when exposed to moist air, gives off fumes colored purple by permanganic acid, and is instantly decomposed by water into permanganic and hydrochloric acids. It is regarded by Dumas, who discovered it, as the heptachloride of manganese; but H. Rose regards it as an oxychloride, $MnCl_2O_2$, analogous to chromic oxychloride, a view which is corroborated by its mode of formation.

Fluorides of manganese have been formed analogous to each of these chlorides.

Manganese Oxides. — Manganese forms four well-defined oxides, constituted as follows: —

Monoxide, or Manganous oxide	MnO
Trimangano-tetroxide, or Manganoso-manganic oxide	Mn_3O_4
Sesquioxide, or Manganic oxide	Mn_2O_3
Dioxide or Peroxide	MnO_2.

The first is a strong base, the third a weak base; the second and fourth are neutral; the second may be regarded as a compound of the first and third, $MnO.Mn_2O_3$. There are also several oxides intermediate between the monoxide and dioxide, occurring as natural minerals or ores of manganese. Manganese likewise forms two series of oxygen salts, called *manganates* and *permanganates*, the composition of which may be illustrated by the potassium salts, viz.:

Potassium manganate . .	$MnO_4K_2 = MnO_3,OK_2$
Potassium permanganate .	$Mn_2O_8K_2 = Mn_2O_7.OK_2$.

The oxides, MnO_3 and Mn_2O_7, corresponding to these salts, are not known.

Monoxide or *Manganous oxide*, MnO. — When manganese carbonate is heated in a stream of hydrogen gas, or vapor of water, carbon dioxide is disengaged, and a greenish powder left behind, which is the monoxide. Prepared at a dull red heat only, the monoxide is so prone to absorb oxygen from the air, that it cannot be removed from the tube without change; but when prepared at a higher temperature, it appears more stable. This oxide is a very powerful base, being isomorphous with magnesia and zinc oxide; it dissolves quietly in dilute acids, neutralizing them completely and forming salts, which have often a beautiful pink color. When alkalies are added to solutions of these compounds, the white hydrated oxide first precipitated speedily becomes brown by passing into a higher state of oxidation.

Sesquioxide or *Manganic oxide*, Mn_2O_3. — This compound occurs in nature as braunite, and in the state of hydrate as manganite: a very beautiful crystallized variety is found at Ilefeld, in the Hartz. It is produced artificially, by exposing the hydrated monoxide to the air, and forms the principal part of the residue left in the iron retort when oxygen gas is prepared by exposing the native dioxide to a moderate red-heat. The

color of the sesquioxide is brown or black, according to its origin or mode of preparation. It is a feeble base, isomorphous with alumina: for, when gently heated with diluted sulphuric acid, it dissolves to a red liquid, which, on the addition of potassium or ammonium sulphate, deposits octohedral crystals having a constitution similar to that of common alum: these are, however, decomposed by water. Strong nitric acid resolves this oxide into a mixture of monoxide and dioxide, the former dissolving, and the latter remaining unaltered; while hot oil of vitriol destroys it by forming manganous sulphate and liberating oxygen gas. On heating it with hydrochloric acid, chlorine is evolved, as with the dioxide, but in smaller amount.

Dioxide, MnO_2. — *Peroxide of manganese. Pyrolusite.* — The most common ore of manganese; it is found both massive and crystallized. It may be obtained artificially in the anhydrous state by gently calcining the nitrate, or in combination with water, by adding solution of bleaching-powder to a salt of the monoxide. Manganese dioxide has a black color, is insoluble in water, and refuses to unite with acids. It is decomposed by hot hydrochloric acid and by oil of vitriol in the same manner as the sesquioxide.

As this substance is an article of commerce of considerable importance, being used in very large quantity for making chlorine, and as it is subject to great alteration of value from admixture of the sesquioxide and several impurities, it becomes desirable to possess means of assaying different samples that may be presented, with a view of testing their fitness for the purposes of the manufacturer. One of the best and most convenient methods is the following: — 50 grains of the mineral, reduced to very fine powder, are put into the little vessel employed in the analysis of carbonates (p. 306), together with about half an ounce of cold water, and 100 grains of strong hydrochloric acid; 50 grains of crystallized oxalic acid are then added, the cork carrying the drying tube is fitted, and the whole quickly weighed or counterpoised. The application of a gentle heat suffices to determine the action; the oxalic acid is oxidized into water and carbon dioxide, which escapes as gas while the manganese remains in solution as manganous chloride:

$$\underset{\text{Manganese dioxide.}}{MnO_2} + \underset{\text{Oxalic acid.}}{C_2O_4H_2} + 2HCl = \underset{\text{Manganese chloride.}}{MnCl_2} + 2OH_2 + \underset{\text{Carbon dioxide.}}{2CO_2}$$

This equation shows that every two molecules of carbon dioxide evolved correspond to one molecule of manganese dioxide decomposed. Now the molecular weight of this oxide, 87, is so nearly equal to twice that of carbon dioxide, 44, that the loss of weight suffered by the apparatus when the reaction has become complete, and the residual gas has been driven off by momentary ebullition, may be taken to represent the quantity of real dioxide in the 50 grains of the sample. It is obvious that the apparatus of Will and Fresenius, described at page 307, may also be used with advantage in this process.

Trimango-tetroxide, or *Red manganese oxide*, Mn_3O_4, or probably $MnO.Mn_2O_3$. This oxide is also found native, as hausmannite, and is produced artificially by heating the dioxide or sesquioxide to whiteness, or by exposing the monoxide or carbonate to a red heat in an open vessel. It is a reddish-brown substance, incapable of forming salts, and acted upon by acids in the same manner as the two other oxides already described. Borax and glass in the fused state dissolve this substance, and acquire the color of the amethyst.

Varvicite, $Mn_4O_7.OH_2$ or $MnO.3MnO_2.OH_2$, is a natural mineral, discovered by Mr. Phillips among certain specimens of manganese ore from Warwickshire: it has also been found at Ilefeld. It much resembles the dioxide, but is harder and more brilliant. By a strong heat, varvicite is converted into red oxide, with disengagement of aqueous vapor and oxygen gas.

Several other oxides, intermediate in composition between the monoxide and dioxide, also occur native; they are probably mere mixtures, and in many cases the monoxide is more or less replaced by the corresponding oxides of iron, cobalt, and copper.

Manganous Sulphate, $SO_4Mn.7OH_2 = SO_3.MnO.7OH_2$.—A beautiful rose-colored and very soluble salt, isomorphous with magnesium sulphate. It is prepared on the large scale for the use of the dyer, by heating in a close vessel manganese dioxide and coal, and dissolving the impure monoxide thus obtained in sulphuric acid, with addition of a little hydrochloric acid towards the end of the process. The solution is evaporated to dryness, and again exposed to a red heat, by which ferric sulphate is decomposed. Water then dissolves out the pure manganese sulphate, leaving ferric oxide behind. The salt is used to produce a permanent brown dye, the cloth steeped in the solution being afterwards passed through a solution of bleaching-powder, by which the monoxide is changed to insoluble hydrate of the dioxide. Manganese sulphate sometimes crystallizes with 5 molecules of water. It forms a double salt with potassium sulphate, containing $(SO_4)_2Mn''K_2.6OH_2$.

Manganese Carbonate, $CO_3Mn'' = CO_2Mn''O$. —Prepared by precipitating the dichloride with an alkaline carbonate. It is an insoluble white powder, sometimes with a buff-colored tint. Exposed to heat, it loses carbon dioxide and absorbs oxygen.

Manganates.—When an oxide of manganese is fused with potash, oxygen is taken up from the air, and a deep green saline mass results, which contains *potassium manganate*, MnO_4K_2 or $MnO_3.OK_2$. The addition of potassium nitrate, or chlorate, facilitates the reaction. Water dissolves this compound very readily, and the solution, concentrated by evaporation in a vacuum, yields green crystals. *Barium manganate*, MnO_4Ba'', is formed in a similar manner.

Permanganates.—When potassium manganate, free from any great excess of alkali, is put into a large quantity of water, it is resolved into hydrated manganese dioxide which subsides, and *potassium permanganate*, $Mn_2O_8K_2$, or $Mn_2O_7.OK_2$, which remains in solution, forming a deep-purple liquid:

$$3MnO_4K_2 + 2OH_2 = MnO_2 + 4OKH + Mn_2O_8K_2.$$

This effect is accelerated by heat. The changes of color accompanying this decomposition are very remarkable, and have procured for the manganate the name *mineral chameleon;* excess of alkali hinders the reaction in some measure, by conferring greater stability on the manganate. Potassium permanganate is easily prepared on a considerable scale. Equal parts of very finely powdered manganese dioxide and potassium chlorate are mixed with rather more than one part of potassium hydrate dissolved in a little water, and the whole is exposed, after evaporation to dryness, to a temperature just short of ignition. The mass is treated with hot water, the insoluble oxide separated by decantation, and the deep-purple liquid concentrated by heat, until crystals form upon its surface: it is then left to cool. The crystals have a dark-purple color, and are not very soluble in cold water. The manganates and permanganates are decomposed by contact with organic matter: the former are said to be isomorphous with the sulphates, and the latter with the perchlorates. The green and red disinfecting agents, known as Condy's fluids, are alkaline manganates and permanganates.

Hydrogen permanganate, or *Permanganic acid*, $Mn_2O_8H_2$, is obtained by dis-

solving potassium permanganate in hydrogen sulphate (SO_4H_2) diluted with one molecule of water, and distilling the solution at 60°–70°. Permanganic acid then passes over in violet vapors, and condenses to a greenish-black liquid, which has a metallic lustre, absorbs moisture greedily from the air, and acts as a most powerful oxidizing agent, instantly setting fire to paper and to alcohol.*

Manganous salts are very easily distinguished by reagents. The *fixed caustic alkalies* and *ammonia* give white precipitates, insoluble in excess, quickly becoming brown. The *carbonates of the fixed alkalies*, and *carbonate of ammonia*, give white precipitates, but little subject to change, and insoluble in excess of carbonate of ammonia. *Hydrogen sulphide* gives no precipitate, but *ammonium sulphide* throws down insoluble flesh-colored sulphide of manganese, which is very characteristic. *Potassium ferrocyanide* gives a white precipitate.

Manganese is also easily detected by the blowpipe: it gives with borax an amethyst-colored bead in the outer or oxidizing flame, and a colorless one in the inner flame. Heated upon platinum foil with sodium carbonate, it yields a green mass of sodium manganate.

URANIUM.

Atomic weight, 120. Symbol, U.

This metal is found in a few minerals, as pitchblende, which is an oxide, and uranite, which is a phosphate; the former is its principal ore. The metal itself is isolated by decomposing the chloride with potassium or sodium, and is obtained as a black coherent powder, or in fused white malleable globules, according to the manner in which the process is conducted. It is permanent in the air at ordinary temperatures, and does not decompose water; but in the pulverulent state it takes fire at 207°, burning with great splendor and forming a dark-green oxide. It unites, also, very violently with chlorine and with sulphur.

Uranium forms two classes of compounds: viz., the *uranous compounds*, in which it is bivalent, *e.g.*, $U''Cl_2$, $U''O$, $U''SO_4$, &c., and the *uranic compounds*, in which it is apparently trivalent, like iron in the ferric compounds, *e.g.*:

$$U'''_2O''_3, \quad U'''_2O''_2Cl_2, \quad U'''_2O''_2(NO_3)_2, \quad U'''_2O''_2(SO_4)''.$$

There are also two oxides intermediate between uranous and uranic oxide. There is no chloride, bromide, iodide, or fluoride corresponding to uranic oxide, such as U_2Cl_6; neither are there any normal uranic oxysalts analogous to the normal ferric salts, such as $U'''_2(NO_3)_6$, $U'''_2(SO_4)''_3$, &c.; but all the uranic salts contain the group U_2O_2, which may be regarded as a bivalent radical (uranyl), uniting with acids in the usual proportions and forming normal salts; thus:

Uranic oxide or Uranyl oxide . . .	$(U_2O_2)''O$
Uranic oxychloride or Uranyl chloride .	$(U_2O_2)''Cl_2$
Uranic nitrate or Uranyl nitrate . . .	$(U_2O_2)''(NO_3)_2$
Uranic sulphate or Uranyl sulphate . .	$(U_2O_2)''(SO_4)''$.

This view of the composition of the uranic salts is not, however, essential,

* Terreil, Bulletin de la Société Chimique de Paris, 1862, p. 40.

since they may also be formulated as basic salts in the manner above illustrated.

Chlorides. — *Uranous chloride*, $U''Cl_2$, is formed, with vivid incandescence, by burning metallic uranium in chlorine gas, also by igniting uranous oxide in hydrochloric acid gas. It crystallizes in dark-green regular octohedrons, and dissolves easily in water, forming an emerald-green solution, which is decomposed when dropped into boiling water, giving off hydrochloric acid and yielding brown precipitate of hydrated uranous oxide. It is a powerful deoxidizing agent, reducing gold and silver, converting ferric salts into ferrous salts, &c.

Uranic oxychloride or *Uranyl chloride*, $U_2O_2Cl_2$, is formed when dry chlorine gas is passed over red-hot uranous oxide, as an orange-yellow vapor, which solidifies to a yellow crystalline fusible mass, easily soluble in water. It forms double salts with the chlorides of the alkali-metals, the potassium salt, for example, having the composition $U_2O_2Cl_2.2KCl.2OH_2$.

Oxides. — *Uranous oxide*, $U''O$, formerly mistaken for metallic uranium, is obtained by heating the oxide, U_3O_4, or uranic oxalate, in a current of hydrogen. It is a brown powder, sometimes highly crystalline. In the finely divided state it is pyrophoric. It dissolves in acids, forming green salts.

Uranoso-uranic oxide, $U_3O_4 = UO.U_2O_3$. — This oxide, analogous to the magnetic oxide of iron, forms the chief constituent of pitchblende. It is obtained artificially by igniting the metal or uranous oxide in contact with the air, or by gentle ignition of uranic oxide or uranic nitrate. It forms a dark-green velvety powder, of specific gravity 7·1 to 7·3. When ignited in hydrogen, or with sodium, charcoal, or sulphur, it is reduced to uranous oxide. When ignited alone, it yields a black oxide, U_4O_5, which is most probably a mixture of uranoso-uranic and uranous oxide. Uranoso-uranic oxide dissolves in strong sulphuric or hydrochloric acid, yielding a mixture of uranous and uranic salt; by nitric acid it is oxidized to uranic nitrate.

Uranic oxide, or *Uranyl oxide*, $U_2O_3 = (U_2O_2)''O$. — Uranium and its lower oxides dissolve in nitric acid, forming uranic nitrate; and when this salt is heated in a glass tube till it begins to decompose, at 250°, pure uranic oxide remains in the form of a chamois-yellow powder. Uranic hydrate, $U_2O_3.2OH_2$, cannot be prepared by precipitating a uranic salt with alkalies, inasmuch as the precipitate always carries down alkali with it; but it may be obtained by evaporating a solution of uranic nitrate in absolute alcohol at a moderate heat, till, at a certain degree of concentration, nitrous ether, aldehyde, and other vapors are given off, and a spongy yellow mass remains, which is the hydrate. In a vacuum at ordinary temperatures, or at 100° in the air, it gives off half its water, leaving the monohydrate, $U_2O_3.OH_2$. This hydrate cannot be deprived of all its water without exposing it to a heat sufficient to drive off part of the oxygen, and reduce it to uranoso-uranic oxide.

Uranic oxide and its hydrates dissolve in acids, forming the *uranic salts*. The *nitrate*, $(U_2O_2)''(NO_3)_2.6OH_2$, may be prepared from pitchblende by dissolving the pulverized mineral in nitric acid, evaporating to dryness, adding water, and filtering; the liquid yields, by due evaporation, crystals of uranic nitrate, which are purified by a repetition of the process, and, lastly, dissolved in ether. This latter solution yields the pure nitrate.

Uranates.—Uranic oxide unites with the more basic metallic oxides. The uranates of the alkali-metals are obtained by precipitating a uranic salt with a caustic alkali; those of the earth-metals and heavy metals, by precipitating a mixture of a uranic salt and a salt of the other metal with ammonia, or by igniting a double carbonate or acetate of uranium and the

other metal (calcio-uranic acetate, for example) in contact with the air. The uranates have, for the most part, the composition $2U_2O_3.M_2O$. They are yellow, insoluble in water, soluble in acids. Those which contain fixed bases are not decomposed at a red heat; but at a white heat, the uranic oxide is reduced to uranoso-uranic oxide, or by ignition in hydrogen to uranous oxide; the mass obtained by this last method easily takes fire in contact with the air. *Sodium uranate*, $2U_2O_3.Na_2O$, is much used for imparting a yellowish or greenish color to glass, and as a yellow pigment on the glazing of porcelain. The "uranium-yellow" for these purposes is prepared on the large scale by roasting pitchblende with lime in a reverberatory furnace; treating the resulting calcium uranate with dilute sulphuric acid; mixing the solution of uranic sulphate thus obtained with sodium carbonate, by which the uranium is first precipitated together with other metals, but then redissolved, tolerably free from impurity, by excess of the alkali; and treating the liquid with dilute sulphuric acid which throws down hydrated sodium uranate, $2U_2O_3.Na_2O.6Aq.$ *Ammonium uranate* is but slightly soluble in pure water, and quite insoluble in water containing sal-ammoniac; it may, therefore, be prepared by precipitating a solution of sodium-uranate with that salt. It occurs in commerce as a fine deep-yellow pigment, also called "uranium yellow." This salt when heated to redness leaves pure uranoso-uranic oxide, and may, therefore, serve as the raw material for the preparation of other uranium compounds.

Uranous salts form green solutions, from which *caustic alkalies* throw down a red-brown gelatinous precipitate of uranous hydrate; *alkaline carbonates*, green precipitates, which dissolve in excess, especially of ammonium carbonate, forming green solutions. *Ammonium sulphide* forms a black precipitate of uranous sulphide; *hydrogen sulphide*, no precipitate.

Uranic salts are yellow, and yield with *caustic alkalies* a yellow precipitate of alkaline uranate, insoluble in excess of the reagent. *Alkaline carbonates* form a yellow precipitate consisting of a carbonate of uranium and the alkali-metal, soluble in excess, especially of acid ammonium or potassium carbonate. *Ammonium sulphide* forms a black precipitate of uranic sulphide. *Hydrogen sulphide* forms no precipitate, but reduces the uranic to a green uranous salt. *Potassium ferrocyanide* forms a red-brown precipitate.

All uranium compounds, fused with *phosphorus salt* or *borax* in the outer blowpipe flame, produce a clear yellow glass, which becomes greenish on cooling. In the inner flame the glass assumes a green color, becoming still greener on cooling. The oxides of uranium are not reduced to the metallic state by fusion with sodium carbonate on charcoal.

Uranium compounds are used, as already observed, in enamel painting, and for the staining of glass, uranous oxide giving a fine black color, and uranic oxide a delicate greenish-yellow, highly fluorescent glass. Uranium salts are also used in photography.

INDIUM.

Atomic weight, 74. Symbol, In.

This metal has been recently discovered by Reich and Richter,* in the zinc-blende of Freiberg. Its spectrum is characterized by two indigo-colored lines, one very bright and more refrangible than the blue line of strontium, the other fainter but still more refrangible, approaching the blue line of potassium. It was the production of this peculiar spectrum that

* Journal für praktische Chemie, lxxxix. 441.

led to the discovery of the metal. The ore, consisting chiefly of blende, galena, and arsenical pyrites, was roasted to expel sulphur and arsenic, then treated with hydrochloric acid, and the solution was evaporated to dryness. The impure zinc chloride thus obtained exhibited, when examined by the spectroscope, the first of the indigo lines above mentioned. The chloride was afterwards obtained in a state of greater purity, and from this the hydrate and the metal itself were prepared. The first line then came out with much greater brilliancy, and the second was likewise observed

Indium has hitherto been obtained in very small quantity only, so that its properties have been but imperfectly studied. It appears, however, to belong to the iron group. The metal itself is of a lead-gray color, soft, very malleable, and marks paper like lead. It dissolves easily in hydrochloric acid, forming a deliquescent chloride. From the solution of this salt, it is precipitated by ammonia and potash as a hydrate, insoluble in excess of either reagent. Hydrogen sulphide does not precipitate it from an acid solution. The oxide heated on charcoal with soda, yields a metallic globule, which when reheated oxidizes to a yellowish powder. The compounds of indium impart a violet tint to the flame of a Bunsen's burner.

CLASS V.—PENTAD METALS.

ANTIMONY.

Atomic weight, 122. Symbol, Sb (Stibium).

THIS important metal is found chiefly in the state of sulphide. The ore is freed by fusion from earthy impurities, and is afterwards decomposed by heating with metallic iron or potassium carbonate, which retains the sulphur. Antimony has a bluish-white color and strong lustre; it is extremely brittle, being reduced to powder with the utmost ease. Its specific gravity is 6·8; it melts at a temperature just short of redness, and boils and volatilizes at a white heat. This metal has always a distinct crystalline, platy structure, but by particular management it may be obtained in crystals, which are rhombohedral.* Antimony is not oxidized by the air at common temperatures; when strongly heated, it burns with a white flame, producing oxide, which is often deposited in beautiful crystals. It is dissolved by hot hydrochloric acid, with evolution of hydrogen and production of chloride. Nitric acid oxidizes it to antimonic acid, which is insoluble in that liquid.

Antimony forms two classes of compounds, the antimonious compounds in which it is trivalent, as $Sb'''Cl_3$, Sb'''_2O_3, Sb'''_2S_3, &c., and the antimonic compounds in which it is quinquivalent, as Sb^vCl_5, $Sb^v_2O_5$, $Sb^v_2S_5$, &c.

CHLORIDES.—The *trichloride* or *Antimonious chloride*, $SbCl_3$, formerly called *butter of antimony*, is produced when hydrogen sulphide is prepared by the action of strong hydrochloric acid on antimonious sulphide. The impure and highly acid solution thus obtained is put into a retort and distilled, until each drop of the condensed product, on falling into the aqueous liquid of the receiver, produces a copious white precipitate. The receiver is then changed and the distillation continued. Pure antimonious chloride then passes over, and solidifies on cooling to a white, highly crystalline mass, from which the air must be carefully excluded. The same compound is formed by distilling metallic antimony in powder with 2½ times its weight of corrosive sublimate. Antimonious chloride is very deliquescent: it dissolves in strong hydrochloric acid without decomposition, and the solution poured into water gives rise to a white bulky precipitate, which, after a short time, becomes highly crystalline, and assumes a pale fawn-color. This is the old *powder of Algaroth;* it is a compound of trichloride and trioxide of antimony. Alkaline solutions extract the chloride and leave the oxide. Finely powdered antimony thrown into chlorine gas takes fire.

The *pentachloride*, or *Antimonic chloride*, $SbCl_5$, is formed by passing a stream of chlorine gas over gently heated metallic antimony: a mixture of the two chlorides results, which may be separated by distillation. The pentachloride is a colorless volatile liquid, which forms a crystalline compound with a small portion of water, but is decomposed by a larger quantity into antimonic and hydrochloric acids.

* On electrolyzing a solution of 1 part of tartar-emetic in 4 parts of antimonious chloride by a small battery of two elements, antimony forming the positive, and metallic copper the negative pole, crusts of antimony are obtained which possess the remarkable property of exploding and catching fire when cracked or broken (Gore, Proceedings of the Royal Society, ix. 70).

Antimonious Hydride. Antimonetted Hydrogen. Stibine, SbH_3. — A compound of antimony and hydrogen exists, but has not been isolated: when zinc is put into a solution of antimonious oxide, and sulphuric acid added, part of the hydrogen combines with the antimony, and the resulting gas burns with a greenish flame, giving rise to white fumes of antimonious oxide. When the gas is conducted through a red-hot glass tube of narrow dimensions, or burned with a limited supply of air, as when a cold porcelain surface is pressed into the flame, metallic antimony is deposited. On passing a current of antimonetted hydrogen through a solution of silver nitrate, a black precipitate is obtained, containing $SbAg_3$: from the formation of this compound it is inferred that the gas has the composition SbH_3, analogous to ammonia, phosphine, and arsine. There are also several analogous compounds of antimony with alcohol-radicals, such as *trimethylstibine*, $Sb(CH_3)_3$, *triethylstibine*, $Sb(C_2H_5)_3$, &c.

Oxides. — Antimony forms two oxides, Sb_2O_3 and Sb_2O_5, analogous to the chlorides, the first being a basic and the second an acid oxide, also an intermediate neutral oxide, Sb_2O_4.

The *trioxide*, or *Antimonious oxide*, Sb_2O_3, occurs native, though rarely, as *valentinite* or *white antimony*, in shining white trimetric crystals; also as *senarmontite* in regular octohedrons: it is therefore dimorphous. It may be prepared by several methods: as by burning metallic antimony at the bottom of a large red-hot crucible, in which case it is obtained in brilliant crystals; or by pouring solution of antimonious chloride into water, and digesting the resulting precipitate with a solution of sodium carbonate. The oxide thus produced is anhydrous; it is a pale buff-colored powder, fusible at a red heat, and volatile in a closed vessel, but in contact with air at a high temperature, it absorbs oxygen and becomes changed into the tetroxide. When boiled with cream of tartar (acid potassium tartrate), it is dissolved, and the solution yields on evaporation crystals of *tartar-emetic*, which is almost the only antimonious salt that can bear admixture with water without decomposition. An impure oxide for this purpose is sometimes prepared by carefully roasting the powdered sulphide in a reverberatory furnace, nace, and raising the heat at the end of the process, so as to fuse the product: it has long been known under the name of *glass of antimony*, or *vitrum antimonii*.

Antimonious oxide likewise acts as a feeble acid, forming salts called *antimonites*, which however are very unstable.

The *tetroxide*, or *Antimonoso-antimonic oxide*, $Sb_2O_3 . Sb_2O_5$, occurs native as *cervantite* or *antimony ochre*, in acicular crystals, or as a crust or powder. It is the ultimate product of the oxidation of the metal by heat and air: it is a grayish-white powder, infusible, and non-volatile, insoluble in water and acids, except when recently precipitated. On treating it with tartaric acid (acid potassium tartrate), antimonious oxide is dissolved, antimonic acid remaining behind; and when a solution of the tetroxide in hydrochloric acid is gradually dropped into a large quantity of water, antimonious oxide is precipitated, while antimonic acid remains dissolved. From these and similar reactions it has been inferred that the tetroxide is a compound of the trioxide and pentoxide. On the other hand, it is sometimes regarded as a distinct oxide, because it dissolves without decomposition in alkalies, forming salts (often called *antimonites*), which may be obtained in the solid state. Two potassium salts, for example, have been formed, containing $Sb_2O_4 . K_2O$ and $2Sb_2O_4 . K_2O$; and a calcium salt $2Sb_2O_4 . 3CaO$, occurs as a natural mineral called *romeine*. These salts may, however, be regarded as compounds of antimonates and antimonites (containing Sb_2O_3): thus, $2(Sb_2O_4 . K_2O) = (Sb_2O_5 . K_2O) + (Sb_2O_3 . K_2O)$.

The *pentoxide*, or *Antimonic oxide*, Sb_2O_5, is formed as an insoluble hydrate

when strong nitric acid is made to act upon metallic antimony; and, on exposing this hydrate to a heat short of redness, it yields the anhydrous pentoxide as a pale straw-colored powder, insoluble in water and acid. It is decomposed by a red-heat, yielding the tetroxide.

Hydrated antimonic oxide is likewise obtained by decomposing antimony pentachloride with an excess of water, hydrochloric acid being formed at the same time. The hydrated oxides, or acids, produced by the two processes mentioned, differ in many of their properties, and especially in their deportment with bases. The acid produced by nitric acid, called *antimonic acid*, is monobasic, producing normal salts of the form $Sb_2O_5 . M_2O$, or SbO_3M, and acid salts containing $2Sb_2O_5 . M_2O$, or $Sb_2O_5 . 2SbO_3M$. The other, called *metantimonic acid*, is bibasic, forming normal salts containing $Sb_2O_5 . 2M_2O$, or $Sb_2O_7M_4$, and acid salts, containing $2Sb_2O_5 . 2M_2O$, or $Sb_2O_5 . M_2O$, so that the acid metantimonates are isomeric or polymeric, with the normal antimonates. Among the metantimonates an acid potassium salt, $Sb_2O_5 . K_2O . 7OH$, is to be particularly noticed as yielding a precipitate with sodium salts: it is, indeed, the only reagent which precipitates sodium. It is obtained by fusing antimonic oxide with an excess of potash in a silver crucible, dissolving the fused mass in a small quantity of cold water, and allowing it to crystallize in a vacuum. The crystals consist of normal potassium metantimonate, $Sb_2O_5 . 2KO$, and, when dissolved in pure water, are decomposed into free potash and acid metantimonate.

Sulphides. The *trisulphide* or *Antimonious sulphide*, Sb_2S_3, occurs native as a lead-gray, brittle substance, having a radiated crystalline texture, and is easily fusible. It may be prepared artificially by melting together antimony and sulphur. When a solution of tartar-emetic is precipitated by hydrogen sulphide, a brick-red precipitate falls, which is the same substance combined with a little water. If the precipitate be dried and gently heated, the water may be expelled without other change of color than a little darkening, but at a higher temperature it assumes the color and aspect of the native sulphide. This remarkable change probably indicates a passage from the amorphous to the crystalline condition.

When powdered antimonious sulphide is boiled in a solution of caustic potash, it is dissolved antimonious oxide, and potassium sulphide being produced, the latter unites with an additional quantity of antimonious sulphide to form a soluble sulphur-salt, in which the potassium sulphide is the sulphur base, and the antimonious sulphide is the sulphur acid:

$$3K_2O + 2Sb_2S_3 = Sb_2O_3 + Sb_2S_3 . 3K_2S.$$

The antimonious oxide separates in small crystals from the boiling solution when the latter is concentrated, and the sulphur-salt dissolves an extra portion of antimonious sulphide, which it again deposits on cooling as a red amorphous powder, containing a small admixture of antimonious oxide and potassium sulphide. This is the *kermes mineral* of the old chemists. The filtered solution mixed with an acid gives a potassium salt, hydrogen sulphide, and precipitated antimonious sulphide. Kermes may also be made by fusing a mixture of 5 parts antimonious sulphide and 3 of dry sodium carbonate, boiling the mass in 80 parts of water, and filtering while hot: the compound separates on cooling. The compounds of antimonious sulphide with basic sulphides are called *sulph-antimonites;* many of them occur as natural minerals. For example: zinkenite, $Sb_2S_3 . PbS$; feather ore, $Sb_2S_3 . 2PbS$; boulangerite, $Sb_2S_3 . 3PbS$; fahlore, or tetrahedrite, $Sb_2S_3 . 4Cu_2S$, the antimony being more or less replaced by arsenic, and the copper by silver, iron, zinc, and mercury.

The *pentasulphide* or *Antimonic sulphide*, Sb_2S_5, formerly called *sulphur auratum*, is also a sulphur acid, forming salts called *sulphantimonates*, most of

which have the composition $Sb_2S_5 . 3M_2S$, or SbS_4M_3, analogous to the normal orthophosphates and arsenates. When 18 parts finely powdered antimonious sulphide, 17 parts dry sodium carbonate, 13 parts slaked lime, and $3\frac{1}{4}$ parts sulphur, are boiled for some hours in a quantity of water, calcium carbonate, sodium antimonate, antimony pentasulphide, and sodium sulphide are produced. The first is insoluble, and the second partially so: the two last-named bodies, on the contrary, unite to form soluble sodium sulphantimonate, SbS_4Na_3, which may be obtained by evaporation in beautiful crystals. A solution of this substance, mixed with dilute sulphuric acid, furnishes sodium sulphate, hydrogen sulphide, and antimony pentasulphide, which falls as a golden-yellow flocculent precipitate.

The sulphantimonates of the alkali-metals and alkaline earth-metals are very soluble in water, and crystallize for the most part with several molecules of water. Those of the heavy metals are insoluble, and are obtained by precipitation.

The few salts of antimony soluble in water are distinctly characterized by the orange or brick-red precipitate with *hydrogen sulphide*, which is soluble in a solution of ammonium sulphide, and again precipitated by an acid.

Antimonious chloride, as already observed, is decomposed by *water*, yielding a precipitate of oxychloride. The precipitate dissolves in hydrochloric acid, and the resulting solution gives, with *potash*, a white precipitate of trioxide, soluble in a large excess of the reagent; with *ammonia* the same, insoluble in excess; with *potassium* or *sodium carbonate*, also a precipitate of trioxide, which dissolves in excess, especially of the potassium salt, but reappears after a while. If, however, the solution contains *tartaric acid*, the precipitate formed by potash dissolves easily in excess of the alkali; ammonia forms but a slight precipitate, and the precipitates formed by alkaline carbonates are insoluble in excess. The last-mentioned characters are likewise exhibited by a solution of tartar-emetic (potassio-antimonious tartrate). *Zinc* and *iron* precipitate antimony from its solutions as a black powder. *Copper* precipitates it as a shining metallic film, which may be dissolved off by potassium permanganate, yielding a solution which will give the characteristic red precipitate with hydrogen sulphide.

Solid antimony compounds fused upon charcoal with sodium carbonate or potassium cyanide, yield a brittle globule of antimony, a thick white fume being at the same time given off, and the charcoal covered to some distance around with a white deposit of oxide.

Besides its application to medicine, antimony is of great importance in the arts, inasmuch as, in combination with lead, it forms *type-metal*. This alloy expands at the moment of solidifying, and takes an exceedingly sharp impression of the mould. It is remarkable that both its constituents shrink under similar circumstances, and make very bad castings.

Britannia metal is an alloy of 9 parts tin and 1 part antimony, frequently also containing small quantities of copper, zinc, or bismuth. An alloy of 12 parts tin, 1 part antimony, and a small quantity of copper, forms a superior kind of pewter. Alloys of antimony with tin, or tin and lead, are now much used for machinery-bearings in place of gun-metal. Alloys of antimony with nickel and with silver occur as natural minerals.

Antimony trisulphide enters into the composition of the blue signal-lights used at sea.*

* Blue or Bengal light:

Dry potassium nitrate . . .	6 parts
Sulphur	2 "
Antimony trisulphide	1 part.

All in fine powder, and intimately mixed.

ARSENIC.

Atomic weight, 75. Symbol, As.

Arsenic is sometimes found native: it occurs in considerable quantity as a constituent of many minerals, combined with metals, sulphur and oxygen. In the oxidized state it has been found in very minute quantity in a great many mineral waters. The largest proportion is derived from the roasting of natural arsenides of iron, nickel, and cobalt. The operation is conducted in a reverberatory furnace, and the volatile products are condensed in a long and nearly horizontal chimney, or in a kind of tower of brickwork, divided into numerous chambers. The crude arsenious oxide thus produced is purified by sublimation, and then heated with charcoal in a retort; the metal is reduced, and readily sublimes.

Arsenic has a steel-gray color, and high metallic lustre: it is crystalline and very brittle; it tarnishes in the air, but may be preserved unchanged in pure water. Its density, in the solid state, is 5·7 to 5 9. When heated, it volatilizes without fusion, and if air be present, oxidizes to arsenious oxide. Its vapor density, compared with that of hydrogen, is 150, which is twice its atomic weight, so that its molecule in the gaseous state, like that of phosphorus, occupies only half the volume of a molecule of hydrogen (p. 228). The vapor has the odor of garlic.

Arsenic combines with metals in the same manner as sulphur and phosphorus, which it resembles, especially the latter, in many respects: indeed, it is often regarded as a metalloïd.

Arsenic, like nitrogen, behaves in most respects as a triad element, not being capable of uniting with more than three atoms of any one monad element. Thus, it forms the compounds AsH_3, $AsCl_3$, $AsBr_3$, &c., but no compound analogous to the pentachloride of phosphorus or antimony. But just as ammonia, NH_3, can take up the elements of hydrochloric acid to form sal-ammoniac, NH_4Cl, in which nitrogen appears quinquivalent, so likewise can arsenetted hydrogen or arsine, $As'''H_3$, unite with the chlorides, bromides, &c. of the radicals, methyl, ethyl, &c., to form salts in which the arsenic appears to be quinquivalent, *e. g.*:

Arsenethylium bromide . . . $As^{v}H_3(C_2H_5)Br$., &c.
Arsenmethylium chloride . . . $As^{v}H_3(CH_3)Cl$.

In like manner, arsentrimethyl, $As'''(CH_3)_3$, unites with the chlorides of methyl and ethyl, forming the compounds $As^{v}(CH_3)_4Cl$ and $As^{v}(CH_3)_3(C_2H_5)Cl$.

Arsenic likewise forms two oxides, viz., arsenious oxide, As'''_2O_3, and arsenic oxide, $As_{v_2}O_5$, with corresponding acids and salts, analogous to phosphorous and phosphoric compounds; the arsenates, in particular, are isomorphous with the other phosphates, and resemble them closely in many other respects.

Arsenious Chloride, $AsCl_3$. — This, the only known chloride of arsenic, is produced, with emission of heat and light, when powdered arsenic is thrown into chlorine gas. It is prepared by distilling a mixture of 1 part of metallic arsenic and 6 parts of corrosive sublimate, and by distilling arsenious oxide with strong hydrochloric acid, or with a mixture of common salt and sulphuric acid. It is a colorless, volatile, highly poisonous liquid, decomposed by water into arsenious and hydrochloric acids. *Arsenious iodide*, AsI_3, is formed by heating metallic arsenic with iodine: it is a deep-red crystalline substance, capable of sublimation. The corresponding *bromide* and *fluoride* are both liquid.

Hydrides. — Arsenic forms two hydrides, containing 2 and 3 atoms of hydrogen combined with 1 atom of arsenic.

The *trihydride*, *Arsenious hydride*, *Arsenetted hydrogen* or *Arsine*, AsH_3, analogous in composition to ammonia, phosphine, and stibine, is obtained pure by the action of strong hydrochloric acid on an alloy of equal parts of zinc and arsenic, and is produced in greater or less proportion whenever hydrogen is set free in contact with arsenious acid. Arsenetted hydrogen is a colorless gas, of specific gravity 2·695, slightly soluble in water, and having the smell of garlic. It burns, when kindled, with a blue flame, generating arsenious acid. It is also decomposed by transmission through a red-hot tube. Many metallic solutions are precipitated by this substance. When inhaled, it is exceedingly poisonous, even in very minute quantity.

The *dihydride*, AsH_2, or rather $As_2H_4 = \begin{vmatrix} AsH_2 \\ AsH_2 \end{vmatrix}$, is produced by passing an electric current through water, the negative pole being formed of metallic arsenic: also when potassium or sodium arsenide is dissolved in water. It is a brown powder, which gives off hydrogen when heated in a close vessel, and burns when heated in the air. It is analogous in composition to arsendimethyl or cacodyl, $As_2(CH_3)_4$.

Arsenious Oxide, Acid, and Salts. — *Arsenious oxide*, As_2O_3, also called *white oxide of arsenic*, is produced in the manner already mentioned. It is commonly met with in the form of a heavy, white, glassy-looking substance, with smooth conchoïdal fracture, which has evidently undergone fusion. When freshly prepared it is often transparent, but by keeping becomes opaque, at the same time slightly diminishing in density, and acquiring a greater degree of solubility in water. 100 parts of that liquid dissolve at 100° about 11·5 parts of the opaque variety: the largest portion separates, however, on cooling, leaving about 3 parts dissolved: the solution, which contains *arsenious acid*, feebly reddens litmus. Cold water, agitated with powdered arsenious oxide, takes up a still smaller quantity. Alkalies dissolve this substance freely, forming arsenites; compounds with ammonia, baryta, strontia, lime, magnesia, and manganous oxide also have been formed: the silver salt is a beautiful lemon-yellow precipitate. The arsenites are, however, very unstable, and have been but little examined. Those which have the composition AsO_2M, or $As_2O_3 . M_2O$, are generally regarded as normal salts; there are also arsenites containing $As_2O_5M_4$, or $As_2O_3 . 2M_2O$, and AsO_3M_3, or $As_2O_3 . 3M_2O$, besides acid salts. Arsenious oxide is easily soluble in hot hydrochloric acid. Its vapor is colorless and inodorous, and it crystallizes on solidifying in brilliant transparent octohedrons. The oxide or acid itself has a feeble sweetish and astringent taste, and is a most fearful poison.

Arsenic Oxide, Acid, and Salts. — When powdered arsenious oxide is dissolved in hot hydrochloric acid, and oxidized by the addition of nitric acid, the latter being added as long as red vapors are produced, the whole then cautiously evaporated to complete dryness, and the residue heated to low redness, arsenic oxide, As_2O_5, remains in the form of a white anhydrous mass which has no action upon litmus. When strongly heated, it is resolved into arsenious oxide and free oxygen. In water it dissolves slowly but completely, giving a highly acid solution, which, on being evaporated to a syrupy consistence, deposits, after a time, hydrated crystals of arsenic acid, containing $2AsO_4H_3 . OH_2$, or $As_2O_5 . 3OH_2$ + Aq. These crystals, when heated to 100°, give off their water of crystallization and leave *trihydrated arsenic acid*, AsO_4H_3, or $As_2O_5 . 3OH_2$; at 140°—160° the *dihydrate*, $As_2O_7H_4$, or $As_2O_5 . 2OH_2$, is left; and at 260° the monohydrate, AsO_3H, or $As_2O_5 . OH_2$.

The aqueous solutions of the three hydrates and of the anhydrous oxide exhibit exactly the same characters, and all contain the trihydrate, the other hydrates being immediately converted into that compound when dissolved in water; in this respect the hydrates of arsenic acid differ essentially from those of phosphoric acid (p. 285).

Arsenic acid is a very powerful acid, forming salts isomorphous with the corresponding phosphates: it is also tribasic. A *sodium arsenate*, $AsO_4HNa_2.12OH_2$, undistinguishable in appearance from common sodium phosphate, may be prepared by adding the carbonate to a solution of arsenic acid, until an alkaline reaction is apparent, and then evaporating. This salt also crystallizes with 7 molecules of water. Another arsenate, $AsO_4Na_3.12OH_2$, is produced when sodium carbonate in excess is fused with arsenic acid, or when the preceding salt is mixed with caustic soda. A third, $AsO_4H_2Na.OH_2$, is made by substituting an excess of arsenic acid for the solution of alkali. The alkaline arsenates which contain basic water lose the latter at a red heat, but, unlike the phosphates, recover it when again dissolved. The arsenates of the alkalies are soluble in water: those of the earths and other metallic oxides are insoluble, but are dissolved by acid. The precipitate with silver nitrate is highly characteristic of arsenic acid: it is reddish-brown.

Sulphides. — Two sulphides of arsenic are known. The *disulphide*, As_2S_2, occurs native as *Realgar*. It is formed artificially by heating arsenic acid with the proper proportion of sulphur. It is an orange-red, fusible, and volatile substance, employed in painting, and by the pyrotechnist in making *white fire*. The *trisulphide* or *arsenious sulphide*, AsS_3, also occurs native as *Orpiment*, and is prepared artificially by fusing arsenic with the appropriate quantity of sulphur, or by precipitating a solution of arsenious acid with hydrogen sulphide. It is a golden-yellow, crystalline substance, fusible, and volatile by heat. A cold solution of arsenic acid is not immediately precipitated by hydrogen sulphide, but after some hours the solution, saturated with hydrogen sulphide, yields a light-yellow deposit of sulphur, the arsenic acid being reduced to arsenious acid, which is then gradually converted into lemon-yellow arsenious sulphide. In boiling solutions the precipitation takes place immediately. The mixture of sulphur and trisulphide, thus produced, was formerly regarded as a pentasulphide, corresponding to arsenic acid.

The disulphide and trisulphide of arsenic are sulphur-acids, uniting with other metallic sulphides to form sulphur-salts. Those of the disulphide are called *hyposulpharsenites;* they are but little known. The salts of arsenious sulphide are called *sulpharsenites*. Their composition may be represented by that of the potassium salts, viz., As_2S_2K, or $AsS_3.K_2S$; $As_2S_5K_4$, or $As_2S_3.2K_2S$, and AsS_3K_3, or $As_2S_3.3K_2S$. Of these the bibasic salts are the most common. The sulpharsenites of the alkali-metals and alkaline earth-metals are soluble in water, and may be prepared by digesting arsenious sulphide in the solutions of the corresponding hydrates or sulph-hydrates; the rest are insoluble and are obtained by precipitation. Sulphur-salts, called *sulpharsenates*, corresponding in composition to the arsenates, are produced, in like manner, by digesting the mixture of sulphur and arsenious sulphide, precipitated, as above mentioned, from arsenic acid, in solutions of alkaline hydrates or sulph-hydrates; also by passing gaseous hydrogen sulphide through solutions of arsenates. There are three sulph-arsenates of potassium, containing AsS_3K, or $As_2S_5.K_2S$; $As_2S_7K_4$, or $As_2S_5.2K_2S$; and AsS_4K_2, or $As_2S_5.3K_2S$. The sulph-arsenates of the alkali-metals and alkaline earth-metals are soluble in water; the rest are insoluble and are obtained by precipitation.

Arsenious acid is distinguished by characters which cannot be misunderstood.

Silver nitrate, mixed with a solution of arsenious acid in water, occasions no precipitate, or merely a faint cloud: but if a little alkali, or a drop of ammonia, be added, a yellow precipitate of silver arsenite immediately falls. The precipitate is exceedingly soluble in excess of ammonia; that substance must, therefore, be added with great caution; it is likewise very soluble in nitric acid.

Cupric sulphate gives no precipitate with solution of arsenious acid, until the addition has been made of a little alkali, when a brilliant yellow-green precipitate (Scheele's green) falls, which also is very soluble in excess of ammonia.

Hydrogen sulphide passed into a solution of arsenious acid, to which a few drops of hydrochloric or sulphuric acid have been added, occasions the production of a copious bright-yellow precipitate of orpiment, which is dissolved with facility by ammonia, and reprecipitated by acids.

Solid arsenious oxide, heated by the blowpipe in a narrow glass tube with small fragments of dry charcoal, affords a sublimate of metallic arsenic in the shape of a brilliant steel-gray metallic ring. A portion of this, detached by the point of a knife, and heated in a second glass tube, with access of air, yields, in its turn, a sublimate of colorless, transparent, octohedral crystals of arsenious oxide.

All these experiments, which *jointly* give demonstrative proof of the presence of the substance in question, may be performed with perfect precision and certainty upon exceedingly small quantities of material.

The detection of arsenious acid in complex mixtures, containing organic matter and common salt, as beer, gruel, soup, &c., or the fluid contents of the stomach in cases of poisoning, is a very far more difficult problem, but one which is, unfortunately, often required to be solved. These organic matters interfere completely with the liquid tests, and render their indications worthless. Sometimes the difficulty may be eluded by a diligent search in the suspected liquid, and in the vessel containing it, for fragments or powder of solid arsenious oxide, which, from its small degree of solubility, often escape solution, and from the high density of the substance, may be found at the bottom of the vessels in which the fluids are contained. If anything of the kind be found, it may be washed by decantation with a little cold water, dried, and then reduced with charcoal. For the latter purpose, a small glass tube is taken, having the figure represented in the margin; white German glass, free from lead, is to be preferred. The arsenious oxide, or what is suspected to be such, is dropped to the bottom, and covered with splinters or little fragments of charcoal, the tube being filled to the shoulder. The whole is gently heated, to expel any moisture that may be present in the charcoal, and the deposited water wiped from the interior of the tube with bibulous paper. The narrow part of the tube containing the charcoal, from *a* to *b*, is now heated by the blowpipe flame; when red-hot, the tube is inclined, so that the bottom also may become heated. The arsenious oxide, if present, is vaporized, and reduced by the charcoal, and a ring of metallic arsenic deposited on the cool part of the tube. To complete the experiment, the tube may be melted at *a* by the point of the flame, drawn off, and closed, and the arsenic oxidized to arsenious oxide, by chasing it up and down by the heat of a small spirit-lamp. A little water may afterwards be introduced, and boiled in the tube, by which the arsenious oxide will be dissolved, and to this solution the tests of silver nitrate

Fig. 174.

and ammonia, copper sulphate and ammonia, and hydrogen sulphide, may be applied.

When the search for solid arsenious oxide fails, the liquid itself must be examined; a tolerably limpid solution must be obtained, from which the arsenic may be precipitated by hydrogen sulphide, and the orpiment collected, and reduced to the metallic state. It is in the first part of this operation that the chief difficulty is found: such organic mixtures refuse to filter, or filter so slowly as to render some method of acceleration indispensable.* Boiling with a little caustic potash or acetic acid will sometimes effect this object. The following is an outline of a plan which has been found successful in a variety of cases in which a very small quantity of arsenious acid had been purposely added to an organic mixture: — Oil of vitriol, itself perfectly free from arsenic, is mixed with the suspected liquid, in the proportion of about a measured ounce to a pint, having been previously diluted with a little water, and the whole is boiled in a flask for half an hour, or until a complete separation of solid and liquid matter becomes manifest. The acid converts any starch that may be present into dextrin and sugar: it completely coagulates albuminous substances, and casein, in the case of milk, and brings the whole in a very short time into a state in which filtration is both easy and rapid. Through the filtered solution, when cold, a current of hydrogen sulphide is transmitted, and the liquid is warmed, to facilitate the deposition of the arsenious sulphide, which falls in combination with a large quantity of organic matter, which often communicates to it a dirty color. This is collected upon a small filter, and washed. It is next transferred to a capsule, and heated with a mixture of nitric and hydrochloric acids, by which the organic impurities are in great measure destroyed, and the arsenic oxidized to arsenic acid. The solution is evaporated to dryness, the soluble part taken up by dilute hydrochloric acid, and then the solution saturated with sulphurous acid, whereby the arsenic acid is reduced to the state of arsenious acid, the sulphurous being oxidized to sulphuric acid. The solution of arsenious acid may now be precipitated by hydrogen sulphide without any difficulty. The liquid is warmed, and the precipitate washed by decantation, and dried. It is then mixed with *black flux*, and heated in a small glass tube, similar to that already described, with similar precautions; a ring of reduced arsenic is obtained, which may be oxidized to arsenious oxide, and further examined. The black flux is a mixture of potassium carbonate and charcoal, obtained by calcining cream of tartar in a close crucible; the alkali transforms the sulphide into arsenious acid, the charcoal subsequently effecting the deoxidation. A mixture of anhydrous sodium carbonate and charcoal may be substituted with advantage for the common black flux, as it is less hygroscopic.

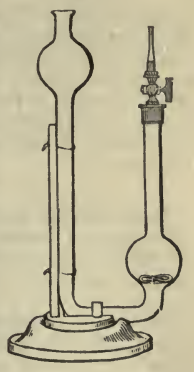
Other methods of proceeding, different in principle from the foregoing, have been proposed, as that of the late Mr. Marsh, which is exceedingly delicate. The suspected liquid is acidulated with sulphuric acid, and placed in contact with metallic zinc; the hydrogen reduces the arsenious acid and combines with the arsenic, if any be present. The gas is burned at a jet, and a piece of glass or porcelain held in the flame, when any admixture of arsenetted hydrogen is at once known by the production of a brilliant black metallic spot of reduced arsenic on the porcelain; or the gas is passed through a glass tube heated at one or two places to redness, whereby the arsenetted hydrogen is decomposed, a ring of metallic arsenic appearing behind the heated portion of the tube.

It has been observed (page 419) that antimonetted hydrogen gives a similar result. In order to distinguish the two substances, the gas may be passed into a solution of silver nitrate. Both gases give rise to a black

* Respecting the separation of the arsenious acid by dialysis, see page 149.

precipitate, which, in the case of antimonetted hydrogen, consists of silver antimonide, Ag_3Sb, whilst in the case of arsenetted hydrogen, it is pure silver, the arsenic being then converted into arsenious acid, which combines with a portion of silver oxide. The silver arsenite remains dissolved in the nitric acid which is liberated by the precipitation of the silver, and may be thrown down with its characteristic yellow color by adding ammonia to the liquid filtered off from the black precipitate. The black silver antimonide, when carefully washed, and subsequently boiled with a solution of tartaric acid, yields a solution containing antimony only, from which hydrogen sulphide separates the characteristic orange-yellow precipitate of antimonious sulphide.

Fig. 175.



A convenient form of Marsh's instrument is that shown in fig. 175: it consists of a bent tube, having two bulbs blown upon it, fitted with a stop-cock and narrow jet. Slips of zinc are put into the lower bulb, which is afterwards filled with the liquid to be examined. On replacing the stop-cock, closed, the gas collects and forces the liquid into the upper bulb, which then acts by its hydrostatic pressure, and expels the gas through the jet so soon as the stop-cock is opened. It must be borne in mind that both common zinc and sulphuric acid often contain traces of arsenic. Mr. Bloxam * has proposed an important modification of Marsh's process for the detection of arsenic and antimony in organic substances, which is based on the behavior of solutions of these metals under the influence of the electric current. Antimony is deposited in the metallic state, without any disengagement of antimonetted hydrogen, while arsenic is evolved as arsenetted hydrogen, which may be recognized by the characters already indicated.

A slip of copper-foil boiled in the poisoned liquid, previously acidulated with hydrochloric acid, withdraws the arsenic, and becomes covered with a white alloy. By heating the metal in a glass tube, the arsenic is expelled, and oxidized to arsenious acid. This is called Reinsch's test.

BISMUTH.

Atomic weight, 210. Symbol, Bi.

Bismuth is found chiefly in the metallic state, disseminated through various rocks, from which it is separated by simple exposure to heat. The metal is highly crystalline and very brittle: it has a reddish-white color, and a density of 9·9. Crystals of great beauty may be obtained by slowly cooling a considerable mass of this substance until solidification has commenced, then piercing the crust, and pouring out the fluid residue. Bismuth melts at about 260° C. (500° F.), and volatilizes at a high temperature. It is remarkable as being the most diamagnetic of all known bodies. It is little oxidized by the air, but burns when strongly heated with a bluish flame. Nitric acid, somewhat diluted, dissolves it freely.

Bismuth forms three classes of compounds, in which it is bi-, tri-, and quinquivalent respectively. The tri-compounds are the most stable and the most numerous. The only known compounds in which bismuth is quinquivalent are indeed the pentoxide, Bi_2O_5, together with the corresponding acid and metallic salts. Nevertheless, bismuth is regarded as a pentad, on

* Journal Chem. Soc., xiii. 338.

account of the analogy of its compound with those of antimony. Several bismuth compounds are known in which the metal is apparently bivalent, but really trivalent, as:

$$Bi_2Cl_4, \text{ or } \begin{matrix} Bi''Cl_2 \\ | \\ Bi''Cl_2 \end{matrix}; \quad Bi_2O_2, \text{ or } \begin{matrix} Bi''O \\ | \\ Bi''O \end{matrix}, \text{ \&c.}$$

Chlorides. — The *trichloride* or *Bismuthous chloride* is formed when bismuth is heated in a current of chlorine gas, and passes over as a white, easily fusible substance, which readily attracts moisture from the air, and is converted into a crystallized hydrate. The same substance is produced when bismuth is dissolved in nitromuriatic acid, and the solution evaporated. Bismuthous chloride dissolves in water containing hydrochloric acid, but is decomposed by pure water, yielding a white precipitate of oxychloride:

$$BiCl_3 + OH_2 = BiClO + 2HCl.$$

The *dichloride*, Bi_2Cl_4, produced by heating the trichloride with metallic bismuth, is a brown, crystalline, easily fusible mass, readily decomposed by water. At a high temperature it is resolved into the trichloride and metallic bismuth.

Oxides. — The *trioxide*, or *Bismuthous oxide*, is a straw-yellow powder, obtained by gently igniting the neutral or basic nitrate. It is fusible at a high temperature, and in that state acts towards siliceous matter as a powerful flux.

The *hydrate*, $Bi'''HO_2$, or $Bi_2O_3 . OH_2$, is obtained as a white precipitate when a solution of the nitrate is decomposed by an alkali. Both the hydrate and the anhydrous oxide dissolve in the stronger acids, forming the bismuthous salts, which have the composition $Bi'''R_3$, where R denotes an acid radical, *e. g.*, $Bi'''Cl_3$, $Bi'''(NO_3)_3$, $Bi'''_2(SO_4)_3$. Many of these salts crystallize well, but cannot exist in solution unless an excess of acid is present. On diluting the solutions with water, a basic salt is precipitated, and an acid salt remains in solution.

The *normal nitrate*, $Bi'''(NO_3)_3 . 5OH_2$, or $Bi_2O_3 . 3N_2O_5 . 10OH_2$, forms large transparent colorless crystals, which are decomposed by water in the manner just mentioned, yielding an acid solution containing a little bismuth, and a brilliant white crystalline powder, which varies to a certain extent in composition according to the temperature and the quantity of water employed, but frequently consists of a basic nitrate, $Bi_2O_3 . N_2O_5 . 2OH_2$, or $Bi'''(NO_3)_3 . Bi_2O_3 . 3OH_2$. A solution of bismuth nitrate, free from any great excess of acid, poured into a large quantity of cold water, yields an insoluble basic nitrate, very similar in appearance to the above, but containing rather a large proportion of bismuth oxide. This basic nitrate was once extensively employed as a cosmetic, but it is said to injure the skin, rendering it yellow and leather-like. It is used in medicine.

Bismuth pentoxide, or *Bismuthic oxide*. — When bismuth trioxide is suspended in a strong solution of potash, and chlorine passed through the liquid, decomposition of water ensues, hydrochloric acid being formed, and the trioxide being converted into the pentoxide. To separate any trioxide that may have escaped oxidation, the powder is treated with dilute nitric acid, when the bismuthic oxide is left as a reddish powder, which is insoluble in water. This substance combines with bases, but the compounds are not very well known. According to Arppe, there is an acid potassium bismuthate containing Bi_2KHO_6, or $2Bi_2O_5 . \left\{ \begin{matrix} K_2O \\ H_2O \end{matrix} \right.$. The pentoxide when heated loses oxygen, an intermediate oxide, Bi_2O_4, being formed, which may be considered as *bismuthous bismuthate*, $2Bi_2O_4 = Bi_2O_3 . Bi_2O_5$.

Bismuth is sufficiently characterized by the decomposition of the nitrate and chloride and by water, and by the black precipitate of bismuth sulphide, insoluble in ammonium-sulphide, which its solutions yield when exposed to the action of hydrogen sulphide.

A mixture of 8 parts of bismuth, 5 parts of lead, and 3 of tin, is known under the name of *fusible metal*, and is employed in taking impressions from dies and for other purposes: it melts below 100°C.

Bismuth is used, in conjunction with antimony, in the construction of thermo-electric piles, these two metals forming the opposite extremes of the thermo-electric series.

VANADIUM.

Atomic weight, 51·2. Symbol, V.

Vanadium is found, in small quantity, in some iron ores, and also as *vanadate of lead*. It has also been discovered in the iron slag of Staffordshire, and recently, by Roscoe,* in larger quantity in the copper-bearing beds at Alderley Edge and Mottram St. Andrews, in Cheshire. Metallic vanadium remains when vanadium nitride is heated to whiteness in ammonia gas, but it does not appear to have been obtained pure. It is described as a white, brittle substance, having a strong lustre, and very refractory in the fire.

Vanadium was, till lately, regarded as a hexad metal, analogous to tangsten and molybdenum; but Roscoe has shown that it is a pentad, belonging to the phosphorus and arsenic group. This conclusion is based upon the composition of the oxides and oxychlorides; and on the isomorphism of the vanadates with the phosphates. The chlorides, and other compounds of vanadium with monad chlorous elements, have not yet been obtained.

Vanadium Oxides.—Vanadium forms four oxides, represented by the formulæ, V_2O_2, V_2O_3, V_2O_4, V_2O_5, analogous therefore to the oxides of nitrogen, excepting that the vanadium oxide analogous to nitrogen monoxide is not yet known.

The *dioxide*, V_2O_2, which was regarded by Berzelius as metallic vanadium, is obtained by reducing either of the higher oxides with potassium, or by passing the vapor of vanadium-oxytrichloride, ($VOCl_3$), mixed with excess of hydrogen, through a combustion-tube containing red-hot charcoal. As obtained by the second process, it forms a light-gray glittering powder, or a metallically lustrous crystalline crust, having a specific gravity of 3·64, brittle, very difficult to fuse, and a conductor of electricity. When heated to redness in the air, it takes fire and burns to black oxide. It is insoluble in sulphuric, hydrochloric, and hydrofluoric acid, but dissolves easily in nitromuriatic acid, forming a dark-blue liquid.

The dioxide may be prepared in solution by the action of nascent hydrogen (evolved by metallic zinc, cadmium, or sodium-amalgam), on a solution of vanadic acid in sulphuric acid. After passing through all shades of blue and green, the liquid acquires a permanent lavender tint, and then contains the vanadium in solution as dioxide, or as *hypo-vanadious* salt. This compound absorbs oxygen more rapidly than any other known agent, and bleaches indigo and other vegetable colors as quickly as chlorine.

Vanadium dioxide may be regarded as entering into many vanadium compounds, as a bivalent radical (just like uranyl in the uranic compounds), and may therefore be called *vanadyl*.

Vanadium trioxide, V_2O_3, or *Vanadyl monoxide*, $(V_2O_2)''O$, is obtained by

* Proceedings of the Royal Society, xvi. 223.

igniting the pentoxide in hydrogen gas, or in a crucible lined with charcoal. It is a black powder, with an almost metallic lustre, and infusible; by pressure it may be united into a coherent mass which conducts electricity. When exposed warm to the air, it glows, absorbs oxygen, and is converted into pentoxide. At ordinary temperatures, it slowly absorbs oxygen, and is converted into tetroxide. By ignition in chlorine gas it is converted into vanadyl-trichloride and vanadium-pentoxide. It is insoluble in acids, but may be obtained in solution by the reducing action of nascent hydrogen (evolved from metallic magnesium) on a solution of vanadic acid in sulphuric acid.

Vanadious oxide, Vanadium tetroxide, or *Vanadyl dioxide*, $V_2O_4 = (V_2O_2)O_2$.— This oxide is produced, either by the oxidation of the dioxide or trioxide, or by the partial reduction of the pentoxide. By allowing the trioxide to absorb oxygen at ordinary temperatures, the tetroxide is obtained in blue shining crystals. It dissolves in acids, the more easily in proportion as it has been less strongly ignited, forming solutions of *vanadious salts*, which have a bright blue color. The same solutions are produced by the action of moderate reducing agents, such as sulphurous, sulph-hydric, or oxalic acid, upon vanadic acid in solution; also by passing air through acid solutions of the dioxide till a permanent blue color is attained. With the *hydrates* and *normal carbonates of the fixed alkalies*, they form a grayish-white precipitate of hydrated vanadious oxide, which dissolves in a moderate excess of the reagent, but is reprecipitated by a large excess in the form of a vanadite of the alkali-metal.

Ammonia in excess produces a brown precipitate, soluble in pure water, but insoluble in water containing ammonia. — *Ammonium sulphide* forms a black-brown precipitate, soluble in excess. — *Tincture of galls* forms a finely divided black precipitate, which gives to the liquid the appearance of ink.

Vanadium-tetroxide also unites with the more basic metallic oxides, forming salts called *vanadites*, all of which are insoluble, except those of the alkali-metals. The solutions of the alkaline vanadites are brown, but when treated with *hydrogen sulphide*, they acquire a splendid red-purple color, arising from the formation of a sulphur-salt. — *Acids* color them blue, by forming a double vanadious salt; *tincture of galls* colors them blackish-blue. The insoluble vanadites, when moistened or covered with water, become green, and are converted into vanadates.

Vanadium pentoxide, Vanadic oxide, or *Vanadyl trioxide*, $V_2O_5 = (V_2O_2)O_3$. This is the highest oxide of vanadium. It may be prepared from native lead vanadate. This mineral is dissolved in nitric acid, and the lead and arsenic are precipitated by hydrogen sulphide, which at the same time reduces the vanadium pentoxide to tetroxide. The blue filtered solution is then evaporated to dryness, and the residue digested in ammonia, which dissolves out the vanadic oxide reproduced during evaporation. In this solution a lump of sal-ammoniac is put; as that salt dissolves, ammonium vanadate subsides as a white powder, being scarcely soluble in a saturated solution of ammonium chloride. By exposure to a temperature below redness in an open crucible, the ammonia is expelled, and vanadic oxide left. By a similar process, Rosco has prepared vanadic oxide from a lime precipitate containing 2 per cent. of vanadium, obtained in working up a poor cobalt ore from Mottram in Cheshire.

Vanadium pentoxide has a reddish-yellow color, and dissolves in 1000 parts of water, forming a light yellow solution. It dissolves also in the stronger acids, forming red or yellow solutions, some of which yield crystalline compounds (vanadic salts) by spontaneous evaporation. It unites, however, with bases more readily than with acids, forming salts called *vanadates*. When fused with alkaline carbonates, it eliminates 3 molecules of carbon dioxide, forming *orthovanadates* analogous to the orthophosphates; thus:

$3(CO_2 . Na_2O)$	+	V_2O_5	=	$V_2O_5 . 3Na_2O$	+	$3CO_2$.
Sodium carbonate.		Vanadic oxide.		Sodium orthovanadate.		Carbon dioxide.

It also forms *metavanadates* analogous to the metaphosphates, and two series of acid *vanadates* or *anhydrovanadates*, viz.:

Lead orthovanadate .	$(VO_4)_2Pb''_3$	or $V_2O_5 . 3Pb''O$
Strontium metavanadate	$(VO_3)_2Sr''$	or $V_2O_5 . Sr''O$
Strontium divanadate	$(VO_3)_2Sr'' . V_2O_5$	or $2V_2O_5 . Sr''O$
Strontium trivanadate	$(VO_3)_2Sr''_4 . 2V_2O_5$	or $3V_2O_5 . Sr''O$.

Lead metavanadate occurs native as *dechenite;* the orthovanadate also, combined with lead chloride, as *vanadinite* or *vanadite*, $PbCl_2 . 3(VO_4)_2Pb_3$, the mineral in which vanadium was first discovered. *Descloizite* is a diplumbic vanadate, $V_2O_7Pb''_2$ or $V_2O_5 . 2PbO$, analogous in composition to a pyrophosphate.

The metavanadates are mostly yellow; some of them, however, especially those of the alkaline earth-metals, and of zinc, cadmium, and lead, are converted by warming — either in the solid state, or under water, or in aqueous solution, especially in presence of a free alkali or alkaline carbonate — into isomeric colorless salts. The same transformation takes place also, though more slowly, at ordinary temperatures. The metavanadates of alkali-metal are colorless. The acid vanadates are yellow, or yellowish-red, both in the solid state and in solution: hence the solution of a neutral vanadate becomes yellowish-red on addition of an acid. The metavanadates of ammonium, the alkali-metals, barium, and lead, are but sparingly soluble in water; the other metavanadates are more soluble. The alkaline vanadates are more soluble in pure water than in water containing free alkali or salt: hence they are precipitated from their solutions by addition of alkali in excess, or of salts. The vanadates are insoluble in alcohol. The aqueous solutions of vanadates form yellow precipitates with *antimony*, *copper*, *lead*, and *mercury* salts: with *tincture of galls*, they form a deep black liquid, which has been proposed for use as vanadium ink.

Hydrogen sulphide reduces them to vanadites, changing the color from red or yellow to blue, and forming a precipitate of sulphur. *Ammonium sulphide* colors the solutions brown-red, and, on adding an acid, a light-brown precipitate is formed consisting of vanadic sulphide mixed with sulphur, the liquid at the same time turning blue. *Hydrochloric acid* decomposes the vanadates, with evolution of chlorine and formation of vanadium tetroxide.

Vanadium Oxychlorides, or Vanadyl Chlorides. — Four of these compounds are known, viz., $VOCl_3$, $VOCl_2$, VOCl, and V_2O_2Cl.

The *oxytrichloride*, $VO'''Cl_3$ (formerly regarded as vanadium trichloride), is prepared:

(1) By the action of chlorine on the trioxide:

$$3V_2O_3 + Cl_{12} = V_2O_5 + 4VOCl_3.$$

(2) By burning the dioxide in chlorine gas, or by passing that gas over an ignited mixture of the trioxide, tetroxide, or pentoxide, and condensing the vapors in a cooled U-tube.

Vanadium oxytrichloride, or vanadyl trichloride, is a golden-yellow liquid, of specific gravity 1·841 at 14·5° C. (58° F.). Boiling point, 127° C. (260° F.). Vapor-density, by experiment, 6·108; by calculation, 6·119. When exposed to the air, it emits cinnabar-colored vapors, being resolved by the moisture of the air into hydrochloric and vanadic acids. It oxidizes magnesium and sodium. Its vapor, passed over perfectly pure carbon at a red heat, yields carbon dioxide; and when passed, together with hydrogen,

through a red-hot tube, yields vanadium trioxide. These reactions show that the compound contains oxygen.

The other oxychlorides of vanadium are solid bodies obtained by partial reduction of the oxytrichloride with zinc or hydrogen.

Vanadium Sulphides. — Two of these compounds are known, analogous to the tetroxide and pentoxide; both are sulphur acids. The *tetrasulphide*, or *Vanadious sulphide*, V_2S_4, is a black substance formed by heating the tetroxide to redness in a stream of hydrogen sulphide; also as a hydrate by dissolving a vanadious salt in excess of an alkaline monosulphide, and precipitating with hydrochloric acid. The *pentasulphide*, or *Vanadic sulphide*, V_2S_5, is formed in like manner by precipitation from an alkaline vanadate.

Vanadium Nitrides.—The *mononitride*, VN, is formed by heating the compound of vanadium oxytrichloride with ammonium chloride to whiteness in a current of ammonia gas. It is a greenish-white powder unalterable in the air. The *dinitride*, VN_2, or V_2N_4, is obtained by exposing the same double salt in ammonia gas to a moderate heat. It is a black powder strongly acted upon by nitric acid. These compounds are of importance, as they promise to yield metallic vanadium, and thence also the chlorides, bromides, &c., of that metal.

All vanadium compounds heated with borax or phosphorus-salt in the outer blow-pipe flame produce a clear bead, which is colorless if the quantity of vanadium is small, yellow when it is large; in the inner flame the bead acquires a beautiful green color.

Vanadic and chromic acids are the only acids whose solutions are red: they are distinguished from one another by the vanadic acid becoming blue, and the chromic acid green, by deoxidation.

When a solution of vanadic acid, or an acidulated solution of an alkaline vanadate, is shaken up with ether containing hydrogen dioxide, the aqueous solution acquires a red color, like that of ferric acetate, while the ether remains colorless. This reaction will serve to detect the presence of 1 part of vanadic acid in 40,000 parts of liquid. The other reactions of vanadium in solution have already been described.

TANTALUM.

Atomic weight, 182. Symbol, Ta.

This metal was discovered, in 1803, by Ekeberg, in two Swedish minerals, tantalite and yttrotantalite. A very similar metal, *columbium*, had been discovered in the preceding year by Hatchett, in columbite from Massachusetts; and Wollaston, in 1807, on comparing the compounds of these metals, concluded that they were identical, an opinion which was for many years received as correct; but their separate identity has been completely established by the researches of H. Rose (commenced in 1846), who gave to the metal from the American and Bavarian columbites, the name *Niobium*, by which it is now universally known. More recently, Marignac has shown that nearly all tantalites and columbites contain both tantalum and niobium (or columbium), some tantalates, from Kimito, in Finland, being, however, free from niobium, and some of the Greenland columbites containing only the latter metal unmixed with tantalum. In all these minerals tantalum exists as a tantalate of iron and manganese; yttrotantalite is essen-

tially a tantalate of yttrium, containing also uranium, calcium, iron, and other metals. Tantalum is also contained in some varieties of wolfram.

Metallic tantalum is obtained by heating the fluotantalate of potassium or sodium with metallic sodium in a well-covered iron crucible, and washing out the soluble salts with water. It is a black powder, which, when heated in the air, burns with a bright light, and is converted, though with difficulty, into tantalic oxide. It is not attacked by sulphuric, hydrochloric, nitric, or even nitromuriatic acid. It dissolves slowly in warm aqueous hydrofluoric acid, with evolution of hydrogen, and very rapidly in a mixture of hydrofluoric and nitric acids.

Tantalum, in its principal compounds, is quinquivalent, the formula of tantalic chloride being $TaCl_5$, that of tantalic fluoride, TaF_5, and that of tantalic oxide (which, in combination with bases, forms the tantalates), Ta_2O_5. There is also a tantalous oxide, said to have the composition TaO_2, and a corresponding sulphide, TaS_2.

Tantalic Chloride.—$TaCl_5$ is obtained, as a yellow sublimate, by igniting an intimate mixture of tantalic oxide and charcoal in a stream of chlorine gas. It begins to volatilize at 144° C. (291° F.) and melts to a yellow liquid at 221° C. (430° F.) The vapor-density between 350° and 440° (662° and 824° F.) has been found by Deville and Troost to be 12·42 referred to air, or 178·9 referred to hydrogen: by calculation, for the normal condensation to two volumes, it is 179·75. Tantalic chloride is decomposed by water, yielding hydrochloric and tantalic acids; but the decomposition is not complete even at the boiling-heat.

Tantalic Fluoride, TaF_5, is obtained in solution by treating tantalic hydrate with aqueous hydrofluoric acid. The solution, mixed with alkaline fluorides, forms soluble crystallizable salts, called *tantalofluorides* or *fluotantalates*. The potassium salt, TaK_2F_7 or $TaF_5.2KF$, crystallizes in monoclinic prisms, isomorphous with the corresponding fluoniobate.

Tantalic Oxide, Ta_2O_5, is produced when tantalum burns in the air, also by the action of water on tantalic chloride, and may be separated as a hydrate from the tantalates by the action of acids. It may be prepared from tantalite, which is a tantalate of iron and manganese, by fusing the finely pulverized mineral with twice its weight of potassium hydrate, digesting the fused mass in hot water, and supersaturating the filtered solution with hydrochloric or nitric acid: hydrated tantalic oxide is then precipitated in white flocks, which may be purified by washing with water.*

Anhydrous tantalic oxide, obtained by igniting the hydrate or sulphate, is a white powder, varying in density from 7·022 to 8·264, according to the temperature to which it has been exposed. Heated in ammonia gas it yields tantalum nitride: heated with carbon bisulphide, it is converted into tantalum bisulphide. It is insoluble in all acids, and can be rendered soluble only by fusion with potassium hydrate or carbonate.

Hydrated Tantalic Oxide, or *Tantalic acid*, obtained by precipitating an aqueous solution of potassium tantalate with hydrochloric acid, is a snow-white bulky powder, which dissolves in hydrochloric and hydrofluoric acids; when strongly heated, it glows and gives off water.

Tantalic oxide unites with basic metallic oxides, forming the tantalates, which are represented by the formulæ, $Ta_2O_5 . M_2O$ and $3Ta_2O_5 . 4M_2O$, the first including the native tantalates, such as ferrous tantalate, and the second certain easily crystallizable tantalates of the alkali-metals. The tantalates of the alkali-metals are soluble in water, and are formed by fusing tantalic oxide with caustic alkalies: those of the earth-metals and heavy metals are insoluble, and are formed by precipitation.

* For more complete methods of preparation, see Watts's Dictionary of Chemistry, vol. v. p. 665.

Tantalum dioxide, or *Tantalous oxide*, TaO_2, may be represented by the formula $\left|\begin{matrix}Ta^{iv}O_2\\ Ta^{iv}O_2\end{matrix}\right.$, in which the metal is still quinquivalent. It is produced by exposing tantalic oxide to an intense heat in a crucible lined with charcoal. It is a hard dark-gray substance, which, when heated in the air, is converted into tantalic oxide.

Hydrochloric, or *sulphuric acid*, added in excess to a solution of alkaline tantalate, forms a precipitate of tantalic acid, which redissolves in excess of the hydrochloric, but not of the sulphuric acid. *Potassium ferrocyanide*, added to a very slightly acidulated solution of an alkaline tantalate, forms a yellow precipitate; the *ferricyanide*, a white precipitate. *Infusion of galls* forms a light-yellow precipitate, soluble in alkalies. When tantalic chloride is dissolved in strong sulphuric acid, and then water and metallic *zinc* are added, a fine blue color is produced, which does not turn brown, but soon disappears.

Tantalic oxide fused with microcosmic salt in either blowpipe flame forms a clear, colorless glass, which does not turn red on addition of a ferrous salt. With borax it also forms a transparent glass, which may be rendered opaque by interrupted blowing, or *flaming*.

NIOBIUM, or COLUMBIUM.

Atomic weight, 94. Symbol, Nb.

This metal, discovered in 1801 by Hatchett, in American columbite, exists likewise, associated with tantalum, in columbites from other sources, and in most tantalites; also, associated with yttrium, uranium, iron, and small quantities of other metals, in Siberian Samarskite, urano-tantalite, or yttroilmenite; also in pyrochlore, euxenite, and a variety of pitchblende from Satersdälen in Norway.

The metal, obtained in the same manner as tantalum, is a black powder, which oxidizes with incandescence when heated in the air. It dissolves in hot hydrofluoric acid, with evolution of hydrogen, and, at ordinary temperatures, in a mixture of hydrofluoric and nitric acid; slowly, also, when heated with strong sulphuric acid. It is oxidized by fusion with acid potassium sulphate, and gradually converted into potassium niobate by fusion with potassium hydrate or carbonate.

Niobium is quinquivalent, and forms only one class of compounds, namely, a chloride, $NbCl_5$; oxide, Nb_2O_5; oxychloride, $NbOCl_3$, &c.

Niobic Oxide, Nb_2O_5, is formed when the metal burns in the air. It is prepared from columbite, &c., by fusing the levigated mineral in a platinum crucible with 6 or 8 parts of acid potassium sulphate, removing soluble salts by boiling the fused mass with water, digesting the residue with ammonium sulphide to dissolve tin and tungsten, boiling with strong hydrochloric acid to remove iron, uranium, and other metals, and finally washing with water. Niobic oxide is thus obtained generally mixed with tantalic oxide, from which it is separated by means of hydrogen and potassium fluoride, $HF.KF$, which converts the tantalum into sparingly soluble potassium tantofluoride, $2KF.TaF_2$, and the niobium into easily soluble potassium nioboxyfluoride, $2KF.NbOF_3.Aq$.

Niobic oxide is also produced by decomposing niobic chloride, or oxychloride, with water: when pure it has a specific gravity of 4·4 to 4·5. It

is an acid oxide, uniting with basic oxides, and forming salts called *niobates*, some of which occur as natural minerals: columbite, for example, being a ferro-manganous niobate. The *potassium niobates* crystallize readily, and in well-defined forms. Marignac has obtained the salts $4K_2O \cdot 3Nb_2O_5 \cdot 16aq.$ crystallizing in monoclinic prisms; $8K_2O \cdot 7Nb_2O_5 \cdot 32aq.$ in pyramidal monoclinic crystals; $3K_2O \cdot 2Nb_2O_5 \cdot 13aq.$ in rhomboïdal prisms; and $K_2O \cdot 3Nb_2O_5 \cdot 5aq.$ as a pulverulent precipitate, by boiling a solution of potassium nioboxy-fluoride with potassium carbonate. The *sodium niobates* are crystalline powders which decompose during washing. There is also a sodium and potassium niobate, containing $Na_2O \cdot 3K_2O \cdot 3Nb_2O_5 \cdot 9aq.$

Niobic Chloride, $NbCl_5$, is obtained, together with the oxychloride, by heating an intimate mixture of niobic oxide and charcoal in a stream of chlorine gas. It is yellow, volatile, and easily fusible. Its observed vapor-density, according to Deville and Troost, is 9·6 referred to air, or 138·6 referred to hydrogen as unity: by calculation for a two-volume condensation, it is $\frac{94 + 5 \cdot 35{\cdot}5}{2} = 135{\cdot}75$. The *oxychloride*, $NbOCl_3$, is white, volatile, but not fusible: its specific gravity, referred to hydrogen, is, by observation, 114·06; by calculation, $\frac{94 + 16 + 3 \cdot 35{\cdot}5}{2} = 109{\cdot}25$. Both these compounds are converted by water into niobic oxide.

Niobic Oxyfluoride, $NbOF_3$, is formed by dissolving niobic oxide in hydrofluoric acid. It unites with the fluorides of the more basic metals, forming salts isomorphous with the titanofluorides, stannofluorides, and tungstofluorides, 1 atom of oxygen in these salts taking the place of 2 atoms of fluorine. Marignac has obtained five potassium nioboxyfluorides, all perfectly crystallized, namely:

$2KF.NbOF_3 . aq.$,	crystallizing in	monoclinic plates;
$3KF.NbOF_3$	"	cuboid forms (systems undetermined),
$3K.HF.NbOF_3$	"	monoclinic needles,
$5KF.3NbOF_3 . aq.$	"	hexagonal prisms,
$4KF.3NbOF_3 . 2aq.$	"	triclinic prisms.

Potassium niobofluoride, $3KF.NbF_5$, separates in shining monoclinic needles from a solution of the first of the nioboxyfluorides above mentioned in hydrofluoric acid. Nioboxyfluorides of ammonium, sodium, zinc, and copper have also been obtained.

The isomorphism of these salts with the stannofluorides, titanofluorides, and tungstofluorides, shows clearly that the existence of isomorphism between the corresponding compounds of any two elements, must not be taken as a decided proof that those elements are of equal atomicity: for in the case now under consideration, we have isomorphous salts formed by tin and titanium, which are tetrads, niobium, which is a pentad, and tungsten, which is a hexad.

The compounds of niobium cannot easily be mistaken for those of any other metal except tantalum. The most characteristic reactions of niobates and tantalates with liquid reagents are the following: —

	Niobates.	*Tantalates.*
Hydrochloric acid . .	White precipitate, insoluble in excess.	White precipitate, soluble in excess.
Ammonium chloride . .	Precipitation slow and incomplete.	Complete precipitation as acid ammonium tantalate.
Potassium ferrocyanide	Red precipitate.	Yellow precipitate.
" ferricyanide .	Bright yellow precipitate.	White precipitate.
Infusion of galls . . .	Orange-red precipitate.	Light yellow precipitate.

Niobic oxide, heated with borax in the outer blow-pipe flame, forms a colorless bead, which, if the oxide is in sufficient quantity, becomes opaque by interrupted blowing or flaming. In microcosmic salt it dissolves abundantly, forming a colorless bead in the outer flame, and in the inner a violet-colored, or if the bead is saturated with the oxide, a beautiful blue bead, the color disappearing in the outer flame

CLASS VI.—HEXAD METALS.

CHROMIUM.

Atomic weight, 52·5. Symbol, Cr.

CHROMIUM is found in the state of oxide, in combination with iron oxide, in some abundance in the Shetland Islands, and elsewhere: as lead chromate it constitutes a very beautiful mineral, from which it was first obtained. The metal itself is prepared in a half-fused condition by mixing the oxide with half its weight of charcoal-powder, enclosing the mixture in a crucible lined with charcoal, and then subjecting it to the very highest heat of a powerful furnace.

Deville has prepared metallic chromium by reducing pure chromium sesquioxide, by means of an insufficient quantity of charcoal, in a lime crucible. Thus prepared, metallic chromium is less fusible than platinum, and as hard as corundum. It is readily acted upon by dilute hydrochloric acid, less so by dilute sulphuric acid, and not at all by concentrated nitric acid. Frémy obtained chromium in small cubic crystals, by the action of sodium vapor on chromium trichloride at a red heat. The crystalline chromium resists the action of concentrated acids, even of nitromuriatic acid.

Chromium forms a hexfluoride, $Cr^{VI}F_6$, and a corresponding oxide, $Cr^{VI}O_3$, analogous to sulphuric oxide; also, an acid, CrO_4H_2, analogous to sulphuric acid, with corresponding salts, the chromates, which are isomorphous with the sulphates. In its other compounds, chromium resembles iron, forming the chromic compounds Cr_2Cl_6, Cr_2O_3, &c., in which it is apparently trivalent but really quadrivalent, and the chromous compounds, $CrCl_2$, CrO, &c., in which it is bivalent.

CHLORIDES. — The *dichloride* or *Chromous chloride*, $CrCl_2$, is prepared by heating the violet-colored trichloride, contained in a porcelain or glass tube, to redness in a current of perfectly dry and pure hydrogen gas: hydrochloric acid is then disengaged, and a white foliated mass is obtained, which dissolves in water with great elevation of temperature, yielding a blue solution, which, on exposure to the air, absorbs oxygen with extraordinary energy, acquiring a deep green color, and passing into the state of chromic oxychloride, $Cr_2Cl_6.Cr_2O_3$. Chromous chloride is one of the most powerful reducing or deoxidizing agents known, precipitating calomel from a solution of mercuric chloride, instantly converting tungstic acid into blue tungsten oxide, and precipitating gold from a solution of auric chloride. It forms, with ammonia, a sky-blue precipitate which turns green on exposure to the air; with ammonia and sal-ammoniac, a blue solution turning red on exposure to the air; and with ammonium sulphide, a black precipitate of chromous sulphide.

The *trichloride* or *Chromic chloride*, Cr_2Cl_6, is obtained in the anhydrous state by heating to redness in a porcelain tube a mixture of chromium sesquioxide and charcoal, and passing dry chlorine gas over it. The trichloride sublimes, and is deposited in the cool part of the tube, in the form

of beautiful crystalline plates of a pale violet color. It is totally insoluble in water under ordinary circumstances, even at the boiling-heat. It dissolves, however, and assumes the deep-green hydrated state in water containing an exceedingly minute quantity of the dichloride in solution. The hydration is marked by the evolution of much heat. This remarkable effect must probably be referred to the class of actions known at present under the name of catalysis.

The green hydrated chromic chloride is easily formed by dissolving chromic hydrate in hydrochloric acid, or by boiling lead chromate, or silver chromate, or a solution of chromic acid, with hydrochloric acid and a reducing agent, such as alcohol, or sulphurous acid, or even with hydrochloric acid:—

$$2CrO_3 + 12HCl = Cr_2Cl_6 + 6OH_2 + Cl_6.$$

The solution thus obtained exhibits the same characters as the chromic oxygen-salts. When evaporated it leaves a dark-green syrup, which, when heated to 100° in a stream of dry air, yields a green mass containing $Cr_2Cl_6.9OH_2$. The same solution evaporated in a vacuum yields green granular crystals containing $Cr_2Cl_6.OH_2$.

Fluorides.—The *trifluoride*, or *Chromic fluoride*, Cr_2F_6, is obtained by treating the dried sesquioxide with hydrofluoric acid, and strongly heating the dried mass, as a dark-green substance, which melts at a high temperature, and sublimes when still more strongly heated, in shining regular octohedrons.

The *hexfluoride*, CrF_6, is formed by distilling lead chromate with fluorspar and fuming oil of vitriol in a leaden retort, and condensing the vapors in a cooled and dry leaden receiver. It then condenses to a blood-red fuming liquid, which volatilizes when its temperature rises a few degrees higher. The vapor is red, and, when inhaled, produces violent coughing and severe oppression of the lungs. The hexfluoride is decomposed by water, yielding hydrofluoric and chromic acids. A fluoride, intermediate in composition between the two just described, is obtained in solution by decomposing the brown dioxide by hydrofluoric acid. The solution is red, and yields by evaporation a rose-colored salt, which is redissolved without alteration by water, and precipitated brown by ammonia.

Oxides.—Chromium forms five oxides, containing CrO, Cr_3O_4, Cr_2O_3, CrO_2, and CrO_3, the first three being analogous in composition to the three oxides of iron.

The *monoxide*, or *Chromous oxide*, $Cr''O$, is formed on adding potash to a solution of chromous chloride, as a brown precipitate, which speedily passes to deep foxy-red, with disengagement of hydrogen, being converted into a higher oxide. Chromous oxide is a powerful base, forming pale-blue salts, which absorb oxygen with extreme avidity. Potassio-chromous sulphate contains $(SO_4)_2{\cdot}Cr''K_2$, like the other members of the same group.

Trichromic tetroxide, $Cr_3O_4 = CrO.Cr_2O_3$, is the above mentioned brownish-red precipitate produced by the action of water upon the monoxide. The decomposition is not complete without boiling. This oxide corresponds with the magnetic oxide of iron, and is not salifiable.

Sesquioxide, or *Chromic oxide*, Cr_2O_3.—When mercurous chromate, prepared by mixing solutions of mercurous nitrate and potassium chromate, or bichromate, is exposed to a red heat, it is decomposed, pure chromium sesquioxide, having a fine green color, remaining. In this state the oxide is, like alumina after ignition, insoluble in acids. The anhydrous sesquioxide may be prepared in a beautifully crystalline form by heating potassium bichromate, $K_2O.2CrO_3$, to full redness in an earthen crucible. One-half of

the chromium trioxide contained in that salt then suffers decomposition, oxygen being disengaged and sesquioxide left. The melted mass is then treated with water, which dissolves out neutral potassium chromate, and the oxide is, lastly, washed and dried. Chromium sesquioxide communicates a fine green tint to glass, and is used in enamel painting. The crystalline sesquioxide is employed in the manufacture of razor-strops. From a solution of chromium sesquioxide in potash, or soda, green gelatinous hydrated sesquioxide of chromium is separated on standing. When finely powdered and dried over sulphuric acid, it consists of $Cr_2O_3.6OH_2$. A hydrate may also be prepared by boiling a somewhat dilute solution of potassium bichromate strongly acidulated with hydrochloric acid, with small successive portions of sugar or alcohol. In the former case carbon dioxide escapes: in the latter, aldehyde and also acetic acid are formed, substances with which we shall become acquainted in organic chemistry; and the chromic acid of the salt becomes converted into chromium trichloride, the color of the liquid changing from red to deep green. The reduction may also be effected, as already observed, by hydrochloric acid alone. A slight excess of ammonia precipitates the hydrate from this solution. It has a pale purplish-green color, which becomes full green on ignition; an extraordinary shrinking of volume and sudden incandescence are observed when the hydrate is decomposed by heat.

Chromium sesquioxide is a feeble base, resembling, and isomorphous with, iron sesquioxide and alumina; its salts (chromic salts) have a green or purple color, and are said to be poisonous.

Chromic sulphate, $(SO_4)_3Cr_2$, is prepared by dissolving the hydrated oxide in dilute sulphuric acid. It unites with the sulphates of potassium and ammonium, giving rise to magnificient double salts, which crystallize in regular octohedrons of a deep claret-color, and possess a constitution resembling that of common alum, the aluminium being replaced by chromium. The ammonium-salt, for example, has the composition $(SO_4)_2Cr'''(NH_4).12$ aq. The finest crystals are obtained by spontaneous evaporation, the solution being apt to be decomposed by heat.

The *dioxide*, CrO_2, which is, perhaps, a chromic chromate, $CrO_3 . Cr_2O_3$, is a brown substance obtained by digesting chromic oxide with excess of chromic acid, or by partial reduction of chromic acid with alcohol, sulphurous acid, &c.

Chromium trioxide, CrO_3; in combination with water, forming *Chromic acid*, $CrO_3 . OH_2 = CrO_4H_2 = (CrO_2)''(OH)_2$. Whenever chromium sesquioxide is strongly heated with an alkali, in contact with air, oxygen is absorbed and the trioxide generated. Chromium trioxide may be obtained nearly pure, and in a state of great beauty, by mixing 100 measures of a cold saturated solution of potassium bichromate with 150 measures of oil of vitriol, and leaving the whole to cool. It crystallizes in brilliant crimson-red prisms: the mother-liquor is poured off, and the crystals are placed upon a tile to drain, being closely covered by a glass or bell-jar.* It is also formed by decomposing the hexfluoride with a small quantity of water. Chromium trioxide is very deliquescent and soluble in water: the solution is instantly reduced by contact with organic matter.

Chromic acid is bibasic and analogous in composition to sulphuric acid; its salts are isomorphous with the corresponding sulphates.

Potassium chromate, CrO_4K_2, or $(CrO_2)''(OK)_2$. — This salt is made directly from the native *chrome-iron-ore*, which is a compound of chromium sesquioxide and ferrous oxide, analogous to magnetic iron ore, by calcination with nitre or with potassium carbonate, or with caustic lime, the ore being reduced to powder and heated for a long time with the alkali in a reverbera-

* Warington, Memoirs of the Chemical Society, i. 18.

tory furnace. The product, when treated with water, yields a yellow solution, which, by evaporation, deposits anhydrous crystals of the same color, isomorphous with potassium sulphate. Potassium chromate has a cool, bitter, and disagreeable taste, and dissolves in 2 parts of water at 15·5°.

Potassium bichromate, or *anhydrochromate*, $2CrO_3 . K_2O$, or $CrO_4K_2 . CrO_3$. — When sulphuric acid is added to the preceding salt in moderate quantity, one half of the base is removed, and the neutral chromate converted into bichromate. The new salt, of which immense quantities are manufactured for use in the arts, crystallizes by slow evaporation in beautiful red tabular crystals, derived from a prism. It melts when heated, and is soluble in 10 parts of water; the solution has an acid reaction.

Potassium trichromate, $3CrO_3 . K_2O$, or $CrO_4K_2 . 2CrO_3$, may be obtained in crystals by dissolving the bichromate in an aqueous solution of chromic acid, and allowing it to evaporate over sulphuric acid.

Lead chromate, CrO_4Pb''. — On mixing solutions of potassium chromate or bichromate with lead nitrate or acetate, a brilliant yellow precipitate falls, which is the compound in question; it is the *chrome-yellow* of the painter. Then this compound is boiled with lime-water, one half of the acid is withdrawn, and a basic lead chromate of an orange-red color left. The basic chromate is also formed by adding lead chromate to fused nitre, and afterwards dissolving out the soluble salts by water: the product is crystalline, and rivals vermilion in beauty of tint. The yellow and orange chrome-colors are fixed upon cloth by the alternate application of the two solutions, and in the latter case by passing the dyed stuff through a bath of boiling lime-water.

Silver chromate, CrO_4Ag_2. — This salt precipitates as a reddish-brown powder when solutions of potassium chromate and silver nitrate are mixed. It dissolves in hot dilute nitric acid, and separates, on cooling, in small ruby-red platy crystals. The chromates of barium, zinc, and mercury are insoluble; the first two are yellow, the last is brick-red.

Chromium Dioxydichloride, CrO_2Cl_2, commonly called *Chlorochromic acid*. — When 3 parts of potassium bichromate and 3½ parts of common salt are intimately mixed and introduced into a small glass retort, 9 parts of oil of vitriol then added, and heat applied as long as dense red vapors arise, this compound passes over as a heavy deep-red liquid resembling bromine: it is decomposed by water, with production of chromic and hydrochloric acids It is analogous to the so-called chloromolybdic, chlorotungstic, and chlorosulphuric acids in composition, and in the products which it yields when decomposed. It may be regarded as formed from the trioxide by substitution of Cl_2 for O, or from chromic acid, $(CrO_2)''(OH)_2$, by substitution of Cl_2 for $(OH)_2$; also as a compound of chromium hexchloride (not known in the separate state), with chromium trioxide: $CrCl_6 . 2CrO_3 = 3CrO_2Cl_2$.

Perchromic Acid is obtained, according to Barreswil, by mixing chromic acid with dilute hydrogen oxide, or potassium bichromate with a dilute but very acid solution of barium dioxide in hydrochloric acid; a liquid is then formed of a blue color, which is removed from the aqueous solution by ether. This very unstable compound has perhaps the composition $Cr_2O_8H_2$ or $Cr_2O_7 . OH_2$, analogous to that of permanganic acid.

Reactions of Chromium compounds. — A solution of chromic chloride or a chromic oxygen salt is not precipitated or changed in any way by hydrogen sulphide. *Ammonium sulphide* throws down a grayish-green precipitate of chromic hydrate. *Caustic fixed alkalies* also precipitate the hydrated oxide, and dissolve it easily when added in excess. *Ammonia*, the same, but nearly

insoluble. The *carbonates of potassium, sodium*, and *ammonium* also throw down a green precipitate of hydrate, slightly soluble in a large excess.

Chromous salts are but rarely meth with; for their reactions, see Chromium dichloride, p. 437.

Chromic acid and its salts are easily recognized in solution by forming a pale yellow precipitate with *barium salts*, bright yellow with *lead salts*, brick-red with *mercurous salts*, and crimson with *silver salts;* also by their capability of yielding the green sesquioxide by reduction.

All chromium compounds, ignited with a mixture of nitre and an alkaline carbonate, yield an alkaline chromate, which may be dissolved out by water, and on being neutralized with acetic acid, will give the reactions just mentioned.

The oxides of chromium and their salts, fused with borax in either blowpipe flame, yield an emerald-green glass. The same character is exhibited by those salts of chromic acid whose bases do not of themselves impart a decided color to the bead. The production of the green color in both flames distinguishes chromium from uranium and vanadium, which give green beads in the inner flame only.

TUNGSTEN, or WOLFRAM.

Atomic weight, 184. Symbol, W.

Tungsten is found, as ferrous tungstate, in the mineral *wolfram*, tolerably abundant in Cornwall; occasionally also as calcium tungstate (*scheelite* or *tungsten*), and as lead tungstate (*scheeletine*). Metallic tungsten is obtained in the state of a dark-gray powder, by strongly heating tungstic oxide in a stream of hydrogen, but requires for fusion an exceedingly high temperature. It is a white metal, very hard and brittle: it has a density of 17·4. Heated to redness in the air, it takes fire and reproduces tungstic oxide.

Tungsten forms two classes of compounds, in which it is quadrivalent and sexvalent respectively, and a third class, of intermediate composition, in which it is apparently quinquivalent.

Chlorides. — These compounds are formed by heating metallic tungsten in chlorine gas. The *hexchloride* or *tungstic chloride*, WCl_6, is also produced, together with oxychloride, by the action of chlorine on an ignited mixture of tungstic oxide and charcoal. The oxychlorides, being more volatile than the hexchloride, may be separated from it by sublimation. The hexchloride forms dark violet scales or fused crusts having a bluish-black metallic iridescence. By contact with water or moist air, it is converted into hydrochloric and tungstic acids. The *tetrachloride*, WCl_4, is formed, according to some authorities, as a dark-red compound, when tungsten is heated in chlorine gas; but according to others, this red compound is a pentachloride, W_2Cl_{10}, or $WCl_4.WCl_6$, the tetrachloride not being known in the separate state.

The *bromides* of tungsten are analogous to the chlorides. — The *hexfluoride*, WF_6, is obtained by evaporating a solution of tungstic acid in hydrofluoric acid.

Oxides. — Tungsten forms three oxides, WO_2, WO_3, and W_2O_5, neither of which exhibits basic properties, so that there are no tungsten salts in which the metal replaces the hydrogen of an acid, or takes the electro-positive part. The trioxide exhibits decided acid tendencies, uniting with basic metallic oxides, and forming crystallizable salts called *tungstates*. The pentoxide may be regarded as a compound of the other two.

The *dioxide*, or *Tungstous oxide*, WO_3, is most easily prepared by exposing tungstic oxide to hydrogen, at a temperature not exceeding dull redness. It is a brown powder, sometimes assuming a crystalline appearance and an imperfect metallic lustre. It takes fire when heated in the air, and burns, like the metal itself, to tungstic oxide. It forms a definite compound with soda.

The *trioxide*, or *Tungstic oxide*, WO_3, is most easily prepared from native calcium tungstate by digestion in nitric or hydrochloric acid, the soluble calcium-salt thereby produced being washed out with water, and the remaining tungstic acid ignited. From wolfram it may be prepared by repeatedly digesting the mineral in strong hydrochloric acid, ultimately with addition of a little nitric acid, to dissolve out the iron and manganese; dissolving the remaining tungstic acid in aqueous ammonia; evaporating to dryness; and heating the residual ammonium tungstate in contact with the air. Tungstic oxide is a yellow powder insoluble in water, and in most acids, but soluble in alkalies. The hot solutions of the resulting alkaline tungstate, when neutralized with an acid, yield a yellow precipitate of *tungstic monohydrate* or *tungstic acid*, WO_4H_2, or $WO_3 . OH_2$. Cold dilute solutions, on the other hand, yield with acids a white precipitate, consisting of *tungstic dihydrate* or *hydrated tungstic acid*, $WO_3 . 2OH_2$, or $WO_4H_2 . OH_2$. Tungstic acid reddens litmus and dissolves easily in alkalis.

Tungstates.—Tungstic acid unites with bases in various, and often in very unusual proportions. It is capable of existing also in two isomeric modifications, viz: 1. *Ordinary tungstic acid*, which is insoluble in water, and forms insoluble salts with all metals, except the alkali-metals and magnesium; 2. *Metatungstic acid*, which is soluble in water, and forms soluble salts with nearly all metals. Ordinary tungstic acid forms normal salts containing WO_4M_2 or $WO_3 . M_2O$, and acid salts containing $7WO_3 . 3M_2O$, which may perhaps be regarded as double salts composed of diacid and triacid tungstates, that is, as $2(2WO_3 . M_2O) + 3WO_3 . M_2O$. The tungstates of potassium and sodium, especially the latter, are sometimes used as mordants in dyeing, in place of stannates; also for rendering muslin and other light fabrics uninflammable. Tungstous tungstate, $WO_3 . WO_2$, which has the composition of *tungsten pentoxide*, W_2O_5, is a blue substance produced by reducing tungstic oxide or tungstic acid with zinc and hydrochloric acid; also by heating ammonium tungstate to redness in a retort.

Metatungstates.—These salts, which have the composition of quadacid tungstates, $4WO_3 . M_2O$, are formed from ordinary tungstates by addition of tungstic acid, or by removing part of the base by means of an acid. They are for the most part soluble and crystallizable. By decomposing barium metatungstate with dilute sulphuric acid, and evaporating the filtrate in a vacuum, hydrated metatungstic acid is obtained in quadratic octohedrons apparently containing $4WO_3 . OH_2 + 31$ aq.; it is very soluble in water.

*Silicotungstates.**—By boiling gelatinous silica with acid potassium tungstate, a crystalline salt is obtained, having the composition of a diacid potassium tungstate, $6(2WO_3 . K_2O)$, or $12WO_3 . K_2O_6$, in which one third of the potassium is replaced by silicium, viz., $12WO_3 . K_8Si^{iv}O_6$, so that the silicium here enters as a *basylous* element. The resulting solution yields with mercurous nitrate a precipitate of *mercurous silicotungstate;* this, when decomposed by an equivalent quantity of hydrochloric acid, yields a solution of *hydrogen silicotungstate* or *silicotungstic acid;* and the other silicotungstates, which are all soluble, are obtained by treating the acid with carbonates.

Silicodecitungstic acid, $10WO_3 . H_8Si^{iv}O_6$, is obtained as an ammonium-salt

* *Marignac*, Ann. Chim. Phys. [4] iii. 5; Watts's Dictionary of Chemistry, v. 913.

by boiling gelatinous silica with solution of acid ammonium tungstate; and from this, the acid and its other salts may be obtained in the same manner as the preceding. The silicodecitungstates are very unstable, and the acid is decomposed by mere evaporation, depositing silica, and being converted into *tungsto-silicic acid*, which is isomeric with silicotungstic acid, and likewise decomposes carbonates. All three of these acids are capable of exchanging either one-half or the whole of their basic hydrogen for metals, thereby forming acid and neutral salts; silicotungstic acid also forms an acid sodium-salt in which only one-fourth of the hydrogen is replaced by sodium.

Tungsten Sulphides. — The *disulphide*, or *Tungstous sulphide*, WS_2, is obtained in soft black needle-shaped crystals by igniting tungsten, or one of its oxides, with sulphur.

The *trisulphide*, or *Tungstic sulphide*, WS_3, is formed by dissolving tungstic acid in ammonium sulphide, and precipitating with an acid, or by adding hydrochloric acid to the solution of an alkaline tungstate saturated with hydrogen sulphide. It is a light-brown precipitate, turning black when dry. It unites easily with basic metallic sulphides, forming the *sulphotungstates*, WS_4M_2, analogous to the normal tungstates.

Reactions of Tungsten compounds. — Soluble tungstates, or metatungstates, supersaturated with sulphuric, hydrochloric, phosphoric, oxalic, or acetic acid, yield, on the introduction of a piece of *zinc*, a beautiful blue color, arising from the formation of blue tungsten oxide. A soluble tungstate, mixed with *ammonium sulphide*, and then with excess of acid, yields a light-brown precipitate of tungstic sulphide, soluble in ammonium sulphide. *Hydrogen sulphide* does not precipitate the acidulated solution of a tungstate, but turns it blue, owing to the formation of the blue oxide. Ordinary tungstates give with *potassium ferrocyanide*, after addition of hydrochloric acid, a brown flocculent precipitate, soluble in pure water free from acid; metatungstates give no precipitate. *Acids* added to solutions of ordinary tungstates, throw down a white or yellow precipitate of tungstic acid; with metatungstates no precipitate is obtained.

All tungsten compounds form colorless beads with borax and phosphorus salt, in the outer blowpipe flame. With *borax*, in the inner flame, they form a yellow glass, if the quantity of tungsten is somewhat considerable, but colorless with a smaller quantity. With *phosphorus salt* in the inner flame they form a glass of a pure blue color, unless metallic oxides are present, which modify it; in presence of iron the glass is blood-red, but the addition of metallic tin renders it blue.

Steel, alloyed with a small quantity of tungsten, acquires extraordinary hardness. Wootz, or Indian steel, contains tungsten. Tungsten has also a remarkable effect on steel in increasing its power of retaining magnetism when hardened. A horse-shoe magnet of ordinary steel weighing two pounds is considered of good quality when it bears seven times its own weight; but, according to Siemens, a similar magnet made with steel containing tungsten may be made to carry twenty times its weight suspended from the armature.*

* Journal of the Chemical Society, July, 1868. 2d Series, vol. vi. p. 284.

MOLYBDENUM.

Atomic weight, 92. Symbol, Mo.

This metal occurs in small quantity as sulphide and as lead molybdate. Metallic molybdenum is obtained by exposing molybdic oxide in a charcoal-lined crucible to the most intense heat that can be obtained. It is a white, brittle, and exceedingly infusible metal, having a density of 8·6, and oxidizing, when heated in the air, to molybdic oxide.

Chlorides. — Molybdenum forms three chlorides, containing $MoCl_2$, Mo_2Cl_6, and $MoCl_4$. The *tetrachloride*, or *molybdic chloride*, is obtained in dark metallically lustrous crystals by passing chlorine in excess over gently heated molybdenum; when heated in a stream of hydrogen, it is reduced to the dark copper-colored *trichloride*, $\left|\begin{matrix}MoCl_3\\MoCl_3\end{matrix}\right|$. The *dichloride*, or *molybdous chloride*, is obtained, though not in the pure state, by exposing the trichloride to a moderate heat in an atmosphere of carbon dioxide, or by heating metallic molybdenum with calomel. In solution it is obtained by saturating hydrochloric acid with molybdous hydrate.

The *bromides* of molybdenum correspond in composition to the chlorides; there is also an oxybromide containing $Mo^{vi}Br_2O_2$.

Fluorides. — Molybdenum forms three fluorides, MoF_2, MoF_4, MoF_6, which are obtained by dissolving the corresponding oxides in hydrofluoric acid. The *hexfluoride* is not known in the free state, but only in combination with basic metallic fluorides and molybdates; thus there is a potassium salt containing $MoO_4K_2 . MoF_8K_2$.

Oxides. — Molybdenum forms the three oxides, $Mo''O$, $Mo^{iv}O_2$, and $Mo^{vi}O_3$, besides several oxides intermediate between the last two, which may be regarded as molybdic molybdates.

The *monoxide*, or *Molybdous oxide*, MoO, is produced by bringing the dioxide or trioxide, in presence of one of the stronger acids, in contact with any of the metals which decompose water. Thus, when zinc is immersed in a concentrated solution of an alkaline molybdate mixed with a quantity of hydrochloric acid sufficient to redissolve the precipitate first thrown down, zinc chloride and molybdous chloride are formed. The dark-colored solution thus obtained is mixed with a large quantity of caustic potash, which precipitates a black hydrated molybdous oxide, and retains the zinc oxide in solution. The freshly precipitated hydrate is soluble in acids and ammonium carbonate; when heated in the air it burns to dioxide, but when dried in a vacuum it leaves the black anhydrous monoxide.

The *dioxide*, or *Molybdic oxide*, MoO_2, is obtained in the anhydrous state by heating sodium molybdate with sal-ammoniac, the molybdic trioxide being reduced to dioxide by the hydrogen of the ammoniacal salt; or, in the hydrated state, by digesting metallic copper in a solution of molybdic acid in hydrochloric acid, until the liquid assumes a red color, and then adding a large excess of ammonia. The anhydrous dioxide is deep brown, and insoluble in acids; the hydrate resembles ferric hydrate, and dissolves in acids, yielding red solutions. It is converted into molybdic acid by strong nitric acid.

Trioxide, MoO_3. — To obtain this oxide (commonly called *Molybdic acid*), native molybdenum sulphide is roasted, at a red heat, in an open vessel, and the impure molybdic trioxide thence resulting is dissolved in ammonia. The filtered solution is evaporated to dryness, and the salt is taken up by

water, and purified by crystallization. It is, lastly, decomposed by heat, and the ammonia expelled. The trioxide may also be prepared by decomposing native lead molybdate with sulphuric acid. It is a white crystalline powder, fusible at a red heat, and slightly soluble in water. The solution contains *molybdic acid;* but this acid, or hydrate, is not known in the solid state. The trioxide is easily dissolved by alkalies, and forms two series of salts. viz., *normal* or *neutral molybdates*, MoO_4R_2, or $MoO_3 . R_2O$, and *anhydromolybdates* or *bimolybdates*, $MoO_4R_2 . MoO_3$, or $2MoO_3 . R_2O$, the symbol R denoting a univalent metal. The neutral molybdates of the alkali-metals are easily soluble in water, and their solutions yield, with the stronger acids, a precipitate either of a less soluble bimolybdate, or of the anhydrous trioxide. The other molybdates are insoluble, and are obtained by precipitation. *Lead molybdate*, Mo_4Pb, occurs native in yellow quadratic plates and octohedrons.

Sulphides. — Molybdenum forms three sulphides, MoS_2, MoS_3, and MoS_4, the last two of which are acid sulphides, forming sulphur-salts. The *disulphide*, or *Molybdic sulphide*, MoS_2, occurs native, as *molybdenite*, in crystallolaminar masses, or tabular crystals, having a strong metallic lustre and lead-gray color, and forming a gray streak on paper like plumbago. The same compound is produced artificially by heating either of the higher sulphides, or by igniting the trioxide with sulphur. When roasted in contact with the air, it is converted into trioxide.

The *trisulphide*, MoS_3, commonly called *sulphomolybdic acid*, is obtained by passing hydrogen sulphide into a concentrated solution of an alkaline molybdate, and precipitating with an acid. It is a black-brown powder, which is dissolved slowly by alkalies, more easily by alkaline sulphides and sulph-hydrates, forming sulphur-salts called *sulphomolybdates*. Most of these salts have the composition MoS_4R_2, or $MoS_3 . R_2S$, analogous to that of the molybdates. The sulpho-molybdates of the alkali-metals, alkaline earth-metals, and magnesium, are soluble in water, forming solutions of a fine red color; the rest are insoluble.

Tetrasulphide, MoS_4. — This is also an acid sulphide, forming salts called *persulphomolybdates*, the general formula of which is MoS_5R_2, or $MoS_4 . R_2S$. The *potassium-salt* is obtained by boiling the sulpho-molybdate with molybdenum trisulphide, washing the resulting precipitate till the wash-water gives a red flocculent precipitate with hydrochloric acid, and then digesting the residue with *cold water*, which dissolves out potassium persulphomolybdate, and leaves the disulphide. The solution of this potassium salt, treated with hydrochloric acid, yields a dark-red precipitate of molybdenum tetrasulphide, which dissolves in alkalies.

Molybdenum in solution is characterized as follows:

Molybdous salts, obtained by dissolving molybdous oxide in acids, are opaque and almost black. They yield, with *hydrogen* sulphide, a brown-black precipitate soluble in ammonium sulphide; with *alkalies* and *alkaline carbonates*, a brownish-black precipitate of molybdous hydrate, easily soluble in acid potassium carbonate, or in ammonium carbonate; with *potassium ferrocyanide*, a dark-brown precipitate; with *sodium phosphate*, a white precipitate.

Solutions of *molybdic salts* have a reddish-brown color. When heated in the air, they have a tendency to become blue by oxidation. In contact with metallic *zinc*, they first blacken and then yield a black precipitate of molybdous hydrate. Their reactions with *alkalies*, *hydrogen sulphide*, &c., are similar to those of molybdous salts; but the precipitates are lighter in color.

Molybdates are colorless unless they contain a colored base. Solutions of the alkaline molybdates yield with *acids* a precipitate of molybdic trioxide, soluble in excess of the precipitant. They are colored yellow by *hydrogen sulphide*, from formation of a sulphomolybdate of the alkali-metal, and then yield with acids a brown precipitate of molybdenum trisulphide. This is an extremely delicate test for molybdic acid. They form white precipitates with the salts of the *earth-metals*, and precipitates of various colors with salts of the *heavy metals; e. g.*, white with lead and silver salts; yellow with ferric salts; and yellowish-white with mercurous salts. When *orthophosphoric acid*, or a liquid containing it, is added to the solution of ammonium molybdate, together with an excess of hydrochloric acid, the liquid turns yellow, and after a while deposits a yellow precipitate of molybdic trioxide, combined with small quantities of phosphoric acid and ammonia. This precipitate is soluble in ammonia and likewise in excess of the phosphate. The reaction is therefore especially adapted for the detection of small quantities of phosphoric acid. The pyrophosphates and metaphosphates do not produce the yellow precipitate. *Arsenic acid* gives a similar reaction.

All the oxides of molybdenum form, with *borax*, in the outer blowpipe flame, a bead which is yellow while hot, and colorless on cooling; in the inner flame, a dark brown bead, which is opaque if excess of molybdenum is present. By long-continued heating, the molybdic oxide may be separated in dark brown flakes, floating in the clear yellow glass. With *phosphorus salt* in the outer flame, all oxides of molybdenum give a bead which is greenish while hot, and colorless on cooling; in the inner flame a clear green bead, from which molybdic oxide cannot be separated by continued heating.

PART III.

ORGANIC CHEMISTRY.

INTRODUCTION.

THE term "Organic Chemistry" originally denoted the chemistry of compounds formed in the bodies of plants and animals. The peculiar characters of the compounds thus formed, and the failure of the earlier attempts to produce them by artificial means, led to the erroneous idea that their formation was due to a mysterious power called "vital force," supposed to reside in the living organism, and to govern all the changes and processes taking place within it. In accordance with this idea, the chemistry of organic compounds, including those which were formed by artificial processes from the products of vegetable and animal life, was erected into a special branch of chemical science.

Later researches have, however, shown that a large number of compounds, formerly regarded as producible only under the influence of the so-called vital force, may be formed either by direct combination of their elements, or by chemical transformation of inorganic compounds.

The first step in the formation of organic compounds from their elements was made by Wöhler, who showed, in 1828, that urea, the characteristic constituent of urine, can be produced by molecular transformation of ammonium cyanate. This experiment, viewed in connection with the fact established about twelve years afterwards, that cyanogen (CN) can be formed by direct combination of its elements, is conclusive of the possibility of forming a product of the living organism from inorganic materials. More recently it has been shown that ethine, or acetylene, C_2H_2, can be produced by the direct combination of carbon and hydrogen; that this compound can be made to take up two additional atoms of hydrogen to form ethene, C_2H_4; and that this latter compound can be converted into alcohol, C_2H_6O, a body formerly supposed to be producible only by the fermentation of sugar; and from this a large number of other compounds can be produced by the action of various reagents. The researches of Berthelot, Kolbe, Wurtz, and other distinguished chemists have led to the discovery of a large number of other cases of the formation of organic compounds, often of great complexity, from substances of purely mineral origin, and ultimately from the elements themselves. The division of compounds into two distinct branches, inorganic and organic — formed according to distinct laws, the former being artificially producible by direct combination of their elements, the latter only under the influence of a supposed vital force — must therefore be abandoned. There is, indeed, but one science of chemistry, of which the study of the compounds called organic forms a part.

Organic chemistry is in fact the chemistry of carbon-compounds, and, in a strictly systematic arrangement, these compounds should be described in connection with the element carbon itself. But the compounds into which

carbon enters are so numerous, their constitution and the transformations which they undergo under the influence of heat and of chemical reagents, are, in many instances, so complicated, that it is found best, for the purposes of instruction, to defer their consideration till the other elements and their compounds have been studied.

It is important, in this place, to mark the distinction between *organic compounds* and *organized bodies*. Organic bodies, such as marsh gas, ethene, benzene, alcohol, sugar, morphine, &c., are definite chemical compounds, many of which, as already observed, may be formed by artificial methods; those which are solid can, for the most part, be crystallized; those which are liquid exhibit constant boiling points. Organized bodies, on the contrary, always consist of mixtures of several definite compounds. They never crystallize, but exhibit a fibrous or cellular structure, and cannot be reduced to the liquid or gaseous state without complete decomposition. Lastly, they are organs, or parts of organs, which are essentially products of vitality, and there is not the slightest prospect of their ever being produced by artificial means.

The study of the composition and chemical relations of organized bodies belongs to a special department of the science called "Physiological Chemistry," which bears the same relation to Organic Chemistry that Chemical Geology bears to Mineralogy.

THE ELEMENTARY OR ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS.

Organic compounds contain, for the most part, only a small number of elements. Many consist only of carbon and hydrogen. A very large number, including most of those which occur ready formed in the bodies of plants and animals, consist of carbon, hydrogen, and oxygen; others consist of carbon, hydrogen, and nitrogen. Others, again, including most of the proximate principles of the animal organism, consist of four elements, carbon, hydrogen, oxygen, and nitrogen. Some contain sulphur, phosphorus, chlorine, and metallic elements; in fact, artificially prepared carbon compounds may contain any elements whatever. Moreover, even those which contain only a small number of elements often exhibit great complexity of structure, in consequence of the accumulation of a large number of carbon-atoms in the same molecule.

Determination of Carbon and Hydrogen. — The quantities of these elements are determined by burning a known weight of the body to be examined, in such a manner as to convert the whole of the carbon into carbon dioxide, and the whole of the hydrogen into water. These products are collected and their weights determined, and from the data thus obtained the quantities of carbon and hydrogen present in the organic substance are calculated. When nitrogen, sulphur, phosphorus, chlorine, &c., are present, special and separate means are resorted to for their estimation.

The method to be described for the determination of the carbon and hydrogen owes its convenience and efficiency to the improvements of Professor Liebig; it has superseded all other processes, and is now invariably employed in inquiries of the kind. With proper care, the results obtained are wonderfully correct; and equal, if not surpass, in precision those of the best mineral analysis. The principle upon which the whole depends is the following: When an organic substance is heated with the oxides of copper, lead, and several other metals, it undergoes complete combustion at the expense of the oxygen of the oxide, the metal being at the same

time reduced either completely, or to a lower state, of oxidation. This effect takes place with the greatest ease and certainty with cupric oxide (black oxide of copper), which, although unchanged by heat alone, gives up oxygen to combustible matter with extreme facility. When nothing but carbon and hydrogen, or those bodies together with oxygen, are present, one experiment suffices; the carbon and hydrogen are determined directly, and the oxygen by difference.

It is of course indispensable that the substance to be analyzed should possess the physical characters of purity, otherwise the inquiry cannot lead to any useful result; if in the solid state, it must also be freed with the most scrupulous care from the moisture which many substances retain with great obstinacy. If it will bear the application of a moderate heat, this desiccation is very easily accomplished by a water or steam bath: in other cases, exposure at common temperatures to the absorbent powers of a large surface of oil of vitriol in the vacuum of an air-pump must be substituted.

Fig. 176.

The operation of weighing the dried powder is conducted in a narrow open tube, about $2\frac{1}{2}$ or 3 inches long; the tube and substance are weighed together, and, when the latter has been removed, the tube with any little adherent matter is re-weighed. This weight, subtracted from the former, gives the weight of the substance employed in the experiment. As only half a gram (5 or 6 grains) is used, the weighings should not involve a greater error than a milligram (or $\frac{1}{500}$ part of a grain).

The copper oxide is best made from the nitrate by complete ignition in an earthen crucible; it is reduced to powder and re-heated just before use, to expel hygroscopic moisture, which it absorbs, even while warm, with avidity. The combustion is performed in a tube of hard white Bohemian glass, having a diameter of 0·4 or 0·5 inch, and in length varying from 14 to 18 inches: this kind of glass bears a moderate red heat without becoming soft enough to lose its shape. One end of the tube is drawn out to a

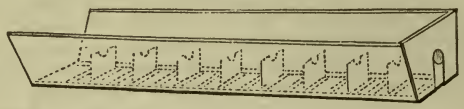
Fig. 177.

point, as shown in fig. 177, and closed; the other is simply heated to fuse and soften the sharp edges of the glass. The tube is now two-thirds filled with the yet warm copper oxide, nearly the whole of which is transferred to a small porcelain or Wedgwood mortar, and very intimately mixed with the organic substance. The mixture is next transferred to the tube, and the mortar rinsed with a little fresh and hot oxide, which is added to the rest; the tube is, lastly, filled to within an inch of the open end with oxide from the crucible. A few gentle taps on the table suffice to shake together the contents, so as to leave a free passage for the evolved gases from end to end. The arrangement of the mixture and oxide in the tube is represented in fig. 177.

The tube is then ready to be placed in the furnace or chauffer: this is constructed of thin sheet iron, and is furnished with a series of supports of equal height, which serve to prevent flexure in the combustion-tube when softened by heat. The chauffer is placed upon flat bricks or a piece of stone, so that but little air can enter the grating, unless the whole be pur-

posely raised. A slight inclination is also given towards the extremity occupied by the mouth of the combustion-tube, which passes through a hole provided for that purpose.

Fig. 178.



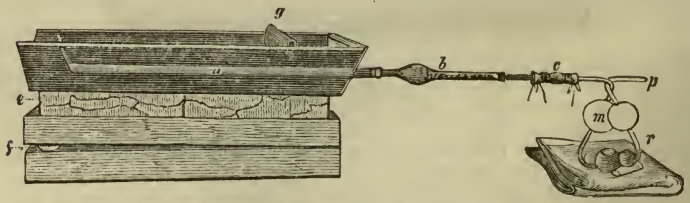
To collect the water produced in the experiment, a small light tube of the form represented in fig. 179, filled with fragments of spongy calcium chloride, is attached by a perforated cork, thoroughly dried, to the open extremity of the combustion-tube. The carbon dioxide is absorbed by a solution of caustic potash, of specific gravity 1·27, which is contained in a small glass apparatus on the principle of a Woulfe's bottle, shown in fig. 180. The connection between the latter and the calcium-chloride tube is

Fig. 180.

Fig. 179.

completed by a little tube of caoutchouc, secured with silk cord. The whole is shown in fig. 181, as arranged for use. Both the calcium-chloride tube and the potash apparatus are weighed with the utmost care before the experiment.

Fig. 181.



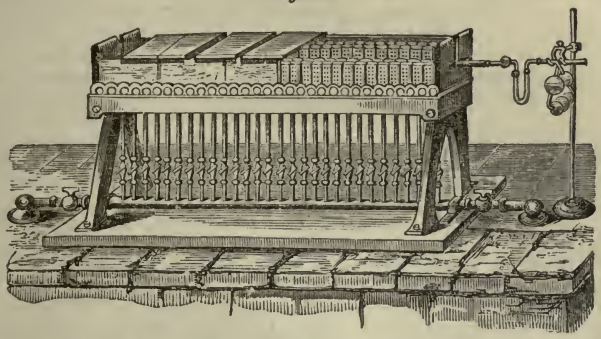
Drawing of the whole arrangement.

The tightness of the junctions may be ascertained by slightly rarefying the included air by sucking a few bubbles from the interior through the liquid, using the dry lips, or, better, a little bent tube with a perforated cork: if the difference of level in the liquid in the two limbs of the potash-apparatus be preserved for several minutes, the joints are perfect. Red-hot charcoal is now placed around the anterior portion of the combustion-tube, containing the pure oxide of copper; and when this is red-hot, the

fire is slowly extended towards the farther extremity by shifting the movable screen represented in the drawing. The experiment must be so conducted that a uniform stream of carbon dioxide shall enter the potash apparatus by bubbles which may be easily counted: when no nitrogen is present, these bubbles are, towards the termination of the experiment, almost completely absorbed by the alkaline liquid, the little residue of air alone escaping. In the case of an azotized body, on the contrary, bubbles of nitrogen gas pass through the potash-solution during the whole process.

When the tube has become completely heated from end to end, and no more gas is disengaged, but, on the other hand, absorption begins be evi-

Fig. 182.



dent, the coals are removed from the farther extremity of the combustion-tube, and the point of the latter broken off. A little air is drawn through the whole apparatus, by which the remaining carbon dioxide and watery vapor are secured. The parts are, lastly, detached, and the calcium-chloride tube and potash-apparatus re-weighed.

Fig. 183.

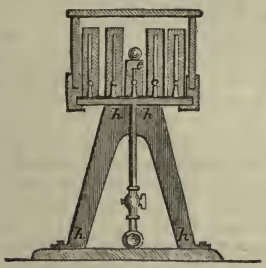
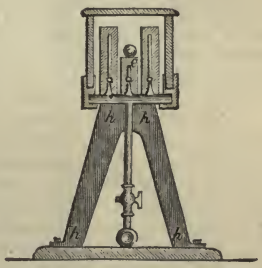


Fig. 184.



The mode of heating the combustion-tube with red-hot charcoal is the original process, and still extensively employed, the construction of the furnace being most simple, and charcoal everywhere accessible. But since the use of coal-gas has been universally adopted in laboratories, many contrivances have been suggested, by means of which this convenient fuel may be employed also in organic analysis. An apparatus of this kind * is the one represented in fig. 182, in which the combustion-tube is heated by a series of perforated clay-burners. These clay-burners are fixed on pipes provided with stopcocks, so that the gas may be lighted according to the requirements of the case. The stopcocks being appropriately adjusted, the

* *Hofmann*, Journal of Chemical Society, vol. xi. p. 30.

gas burns on the surface of the burners with a smokeless blue flame, which renders them in a short time incandescent. The construction of this furnace is readily intelligible by a glance at figures 183 and 184, which exhibit the different parts of the apparatus in section, fig. 183 representing a large furnace with five rows, and fig. 184 a smaller furnace with three rows of clay-burners.

The following account of a real experiment will serve to illustrate the calculation of the results obtained in the combustion of crystallized sugar:

Quantity of sugar employed	4·750 grains.
Potash apparatus weighed after experiment .	781·13
" " before experiment .	773·82
Carbonic dioxide	7·31
Calcium-chloride tube after experiment . .	226·05
" before experiment . .	223·30
Water	2·75

7·31 gr. carbon dioxide = 1·994 gr. carbon: and 2·75 gr. water = 0·3056 gr. hydrogen; or in 100 parts of sugar,*

Carbon	41·98
Hydrogen	6·43
Oxygen, by difference	51·59
	100·00

When the organic substance cannot be mixed with the copper oxide in the manner described, the process must be slightly modified, to meet the particular case. If, for example, a volatile liquid is to be examined, it is enclosed in a little glass bulb with a narrow stem, which is weighed before and after the introduction of the liquid, the point being hermetically sealed. The combustion-tube must have, in this case, a much greater length; and, as the copper oxide cannot be introduced hot, it must be ignited and cooled out of contact with the air, to prevent absorption of watery vapor. This is most conveniently effected by transferring it, in a heated state, to a large platinum crucible to which a closely fitting cover can be adapted. When quite cold, the cover is removed and instantly replaced by a dry glass funnel, by the assistance of which the oxide may be directly poured into the combustion-tube with merely momentary exposure to the air. A little oxide is put in, then the bulb, with its stem broken at *a*, a file-scratch having been previously made; and, lastly, the tube is filled with the cold and dry copper oxide. It is arranged in the chauffer, the calcium-chloride tube and potash apparatus adjusted, and then, some six or eight inches of oxide having been heated to redness, the liquid in the bulb is, by the approximation of a hot coal, expelled, and slowly converted into vapor, which, in passing over the hot oxide, is completely burned. The experiment is then terminated in the usual manner. Fusible fatty substances, and volatile concrete bodies, as camphor, require rather different management, which need not be here described.

Fig. 185.

* The theoretical composition of sugar, $C_{12}H_{22}O_{11}$, reckoned to 100 parts, gives—

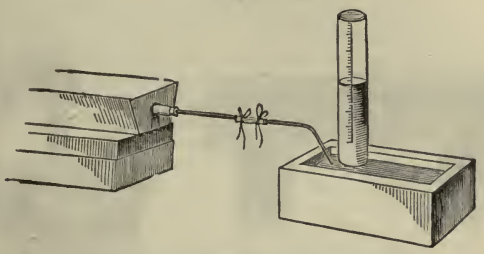
Carbon	42·11
Hydrogen	6·43
Oxygen	51·46
	100·00

Copper oxide which has been used, may be easily restored by moistening with nitric acid, and igniting to redness; it becomes, in fact, rather improved than otherwise, as, after frequent employment, its density is increased and its troublesome hygroscopic powers diminished. For substances which are very difficult of combustion, from the large proportion of carbon they contain, and for compounds into which chlorine enters as a constituent, fused and powdered lead chromate is very advantageously substituted for the copper oxide. Lead chromate freely gives up oxygen to combustible matters, and even evolves, when strongly heated, a little of that gas, which thus ensures the perfect combustion of the organic body.

Analysis of Azotized Substances. — The presence of nitrogen in an organic compound is easily ascertained by heating a small portion with solid potassium hydrate in a test-tube: the nitrogen, if present, is converted into ammonia, which may be recognized by its odor and alkaline reaction. There are several methods of determining the proportion of nitrogen in azotized organic substances, the experimenter being guided in his choice of means by the nature of the substance and its comparative richness in that element. The carbon and hydrogen are first determined in the usual manner, a longer tube than usual being employed, and four or five inches of its anterior portion filled with copper turnings, rendered perfectly metallic by ignition in hydrogen: this serves to decompose any nitrogen oxide that may be formed in the act of combustion. During the experiment, some idea of the abundance or paucity of the nitrogen may be formed, from the number of bubbles of incondensable gas which traverses the solution of potash.

In the case of compounds abounding in nitrogen, and readily burned by

Fig. 186.



copper oxide, a method may be employed, which is very easy of execution: this consists in determining the ratio borne by the liberated nitrogen to the carbon dioxide produced in the combustion. A tube of hard glass, of the usual diameter, and about 15 inches long, is sealed at one end; a little of the organic substance, mixed with copper oxide, is introduced, and allowed to occupy about two inches of the tube; about as much pure oxide is placed over it, and then another portion of a similar mixture; after which the tube is filled up with a second and larger portion of pure oxide, and a quantity of spongy metallic copper. A short bent tube, made movable by a caoutchouc joint, is fitted by a perforated cork, and made to dip into a mercurial trough, while the combustion-tube itself rests in the chauffer (fig. 186).

Fig. 187.

Fire is first applied to the anterior part of the tube containing the metal and unmixed oxide, and, when this is red-hot, to the extreme end. Combustion of the first portion of the mixture takes place, the gaseous products sweeping before them nearly the

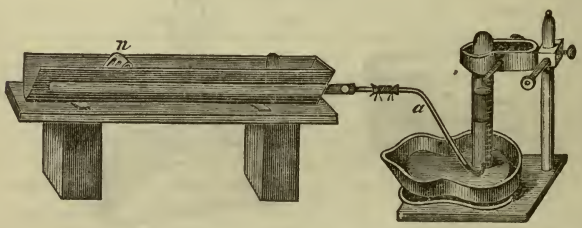
whole of the air of the apparatus. When no more gas issues, the tube is slowly heated by half an inch at a time, in the usual manner, and all the gas very carefully collected in a graduated jar, until the operation is at an end. The volume is then read off, and some strong solution of caustic potash thrown up into the jar by a *pipette* with a curved extremity. When the absorption is complete, the residual volume of nitrogen is observed, and compared with that of the mixed gases, proper correction being made for differences of level in the mercury; and from these data the exact proportion borne by the nitrogen to the carbon can be at once determined.*

If the proportion of nitrogen be but small, the error from the nitrogen of the residual atmospheric air becomes so great as to destroy all confidence in the result of the experiment; and the same thing happens when the substance is incompletely burned by copper oxide: other means must then be employed.

The *absolute* method of determination, also known by the name of Dumas' method, may be had recourse to when the foregoing, or *comparative* method, fails from the first cause mentioned: it gives excellent results, and is applicable to all azotized substances.

A tube of good Bohemian glass, 28 inches long, is securely sealed at one end; into this enough dry acid sodium carbonate is put to occupy 6 inches. A little pure copper oxide is next introduced, and afterwards the mixture of oxide and organic substance, the weight of the latter, between 4·5 and 9 grains, in a dry state, having been correctly determined. The remainder of the tube, amounting to nearly one-half of its length, is then filled up with pure copper oxide and spongy metal, and a round cork, perforated by

Fig. 188.



a piece of narrow tube, is securely adapted to its mouth. This tube is connected by means of a caoutchouc joint with a bent delivery-tube, *a*, and the combustion-tube is arranged in the furnace. A few coals are now ap-

* A molecule of carbon dioxide (CO_2) containing 1 atom of carbon [= 12], occupies the same space as a molecule (or double atom) of nitrogen (NN) [2 . 14 = 28]. If, therefore, the volumes of carbon dioxide and nitrogen in the gaseous mixture are as m : 1, it follows that the number of carbon-atoms in the compound is to the number of nitrogen-atoms as m : 2; and consequently that the weight of the carbon in the compound is to that of the nitrogen as $m \times 12 : 2 \times 14$, or $3\,m : 7$, so that if the percentage of carbon (c) has been previously found, the percentage of nitrogen (n) will be given by the equation:

$$n = \frac{7}{3\,m}\,c.$$

For example, caffeine, which contains 47·48 per cent. of carbon, is found, by the process just described, to yield carbon dioxide and nitrogen in the proportion by volume of 4 : 1; the percentage of nitrogen in caffeine is therefore $\frac{7}{3 \times 4} \times 49{\cdot}48 = 28{\cdot}89$.

plied to the farther end of the tube, so as to decompose a portion of the acid sodium carbonate, the remainder of the carbonate, as well as of the other part of the tube, being protected from the heat by a screen *n*. The current of carbon dioxide thus produced is intended to expel all the air from the apparatus. In order to ascertain that this object, on which the success of the whole operation depends, is accomplished, the delivery-tube is depressed under the level of a mercurial trough, and the gas, which is evolved, collected in a test-tube filled with concentrated potash-solution. If the gas be perfectly absorbed, or if, after the introduction of a considerable quantity, only a minute bubble be left, the air may be considered as expelled. The next step is to fill a graduated glass jar two-thirds with mercury and one-third with a strong solution of potash, and to invert it over the delivery-tube, as represented in fig. 188.

This done, fire is applied to the tube, commencing at the front end, and gradually proceeding to the closed extremity, which still contains some undecomposed acid sodium carbonate. This, when the fire at length reaches it, yields up carbon dioxide, which chases forward the nitrogen lingering in the tube. The carbon dioxide generated during the combustion is wholly absorbed by the potash in the jar, and nothing is left but the nitrogen. When the operation is at an end, the jar, with its contents, is transferred to a vessel of water, and the volume of the nitrogen read off. This is properly corrected for temperature, pressure, and aqueous vapor, and its weight determined by calculation. When the operation has been very successful, and all precautions minutely observed, the result still leaves an error in excess, amounting to 0·3 or 0·5 per cent., due to the residual air of the apparatus, or that condensed in the pores of the copper oxide.

A most elegant process for estimating nitrogen in all organic compounds, except those containing the nitrogen in the form of nitrous acid or nitrogen tetroxide, and in some organic bases, has been put in practice by Will and Varrentrapp. When a non-azotized organic substance is heated to redness with a large excess of potassium or sodium hydrate, it suffers complete and speedy combustion at the expense of the water of the hydrate, the oxygen combining with the carbon of the organic matter to form carbon dioxide, which is retained by the alkali, while its hydrogen, together with that of the substance, is disengaged, sometimes in union with a little carbon. The same change happens when nitrogen is present, but with this addition: the whole of the nitrogen thus abandoned combines with a portion of the liberated hydrogen to form ammonia. It is evident, therefore, that if this experiment be made on a weighed quantity of matter, and circumstances allow the collection of the whole of the ammonia thus produced, the proportion of nitrogen can be easily calculated.

An intimate mixture is made of 1 part caustic soda and 2 or 3 parts quicklime, by slaking lime of good quality with the proper proportion of strong caustic soda, drying the mixture in an iron vessel, and then heating it to redness in an earthen crucible. The ignited mass is rubbed to powder in a warm mortar, and carefully preserved from the air. The lime is useful in many ways: it diminishes the tendency of the alkali to deliquesce, facilitates mixture with the organic substance, and prevents fusion and liquefaction. A proper quantity of the substance to be analyzed, namely, from 5 to 10 grains, is dried and accurately weighed out: this is mixed in a warm porcelain mortar with enough of the soda-lime to fill two-thirds of an ordinary combustion-tube, the mortar being rinsed with a little more of the alkaline mixture, and, lastly, with a small quantity of powdered glass, which completely removes everything adherent to its surface; the tube is then filled to within an inch of the open end with the lime-mixture, and arranged in the chauffer in the usual manner. The ammonia is collected in a little apparatus of three bulbs (fig. 189), containing moderately strong hydrochloric acid, attached by a cork to the combustion-tube.

Matters being thus adjusted, fire is applied to the tube, commencing with the anterior extremity. When it is ignited throughout its whole length, and when no gas issues from the apparatus, the point of the tube is broken, and a little air drawn through the whole. The acid liquid is then emptied into a capsule, the bulbs rinsed into the same, first with a little alcohol, and then repeatedly with distilled water; an excess of pure platinic chloride is added, and the whole evaporated to dryness in a water-bath. The dry mass, when cold, is treated with a mixture of alcohol and ether, which dissolves out the superfluous platinum chloride, but leaves untouched the yellow crystalline ammonium platinochloride. The latter is collected upon a small weighed filter, washed with the same mixture of alcohol and ether, dried at 100° C. (212° F.), and weighed; 100 parts correspond to 6·272 parts of nitrogen. Or, the salt with its filter may be very carefully ignited, the filter burned in a platinum crucible, and the nitrogen reckoned from the weight of the spongy metal, 100 parts of that substance corresponding to 14·18 parts of nitrogen. The former plan is to be preferred in most cases.

Fig. 189.

Bodies very rich in nitrogen, as urea, must be mixed with about an equal quantity of pure sugar, to furnish incondensable gas, and thus diminish the violence of the absorption which otherwise occurs; and the same precaution must be taken, for a different reason, with those which contain little or no hydrogen.

A modification of this process has been suggested by Peligot, which is very convenient if a large number of nitrogen-determinations is to be made. By this plan, the ammonia, instead of being received in hydrochloric acid, is conducted into a known volume (10 to 20 cubic centimetres) of a standard solution of sulphuric acid, contained in the ordinary nitrogen-bulbs. After the combustion is finished, the acid containing the ammonia is poured out into a beaker, colored with a drop of tincture of litmus, and then neutralized with a standard solution of soda in water or of lime in sugar-water, the point of neutralization becoming perceptible by the sudden appearance of a blue tint. The lime-solution is conveniently poured out from the graduated glass tube, described under the head of Alkalimetry. The volume of lime-solution necessary to neutralize the same amount of acid that is used for condensing the ammonia, having been ascertained by a preliminary experiment, it is evident that the difference of the quantities used in the two experiments gives the ammonia collected in the acid during the combustion. The amount of nitrogen may thus be calculated. If, for instance, an acid be prepared, containing 20 grains of pure hydrogen sulphate (SO_4H_2) in 1000 grain-measures — 200 grain-measures of this acid — the quantity introduced into the bulbs — correspond to 1·38 grains of ammonia, or 1·14 grains of nitrogen. The alkaline solution is so graduated that 1000 grain-measures will exactly neutralize the 200 grain-measures of the standard acid. If we now find that the acid, partly saturated with the ammonia disengaged during the combustion of a nitrogenous substance, requires only 700 grain-measures of the alkaline solution, it is evident that $\frac{200 \times 300}{1000} = 60$ grain-measures were saturated by the ammonia, and the quantity of nitrogen is obtained by the proportion — $200 : 1{\cdot}14 = 60 : x$, wherefore $x = \frac{1{\cdot}14 \times 60}{200} = 0{\cdot}342$ grains of nitrogen.

Estimation of Sulphur in Organic Compounds. — When bodies of this class containing sulphur are burned with copper oxide, a small tube containing lead dioxide may be interposed between the calcium-chloride tube and the potash apparatus, to retain any sulphurous acid that may be formed. It is better, however, to use lead chromate in such cases. The proportion of sulphur is determined by oxidizing a known weight of the substance with strong nitric acid, or by fusion in a silver vessel with ten or twelve times its weight of pure potassium hydrate and half as much nitre. The sulphur is thus converted into sulphuric acid, the quantity of which can be determined by dissolving the fused mass in water, acidulating with nitric acid, and adding a barium salt. *Phosphorus* is, in like manner, oxidized to phosphoric acid, the quantity of which is determined by precipitation as ammonio-magnesian phosphate, or otherwise.

Estimation of Chlorine. — The case of a volatile liquid containing chlorine is of very frequent occurrence, and may be taken as an illustration of the general plan of proceeding. The combustion with copper oxide must be very carefully conducted, and two or three inches of the anterior portion of the tube kept cool enough to prevent volatilization of the copper chloride into the calcium-chloride tube. Lead chromate is much better for the purpose. The chlorine is correctly determined by placing a small weighed bulb of liquid in a combustion-tube, which is afterwards filled with fragments of pure quicklime. The lime is brought to a red heat, and the vapor of the liquid driven over it, when the chlorine displaces oxygen from the lime, and gives rise to calcium chloride. When cold, the contents of the tube are dissolved in dilute nitric acid, filtered, and the chlorine precipitated by silver nitrate.

Bromine and *iodine* are estimated in a similar manner.

EMPIRICAL AND MOLECULAR FORMULÆ.

A chemical formula is termed *empirical* when it merely gives the simplest possible expression of the composition of the substance to which it refers. A molecular formula, on the contrary, expresses the absolute number of atoms of each of its elements supposed to be contained in the molecule, as well as the mere relations existing between them. The empirical formula is at once deduced from the analysis of the substance, reckoned to 100 parts; but to determine the molecular formula, other considerations must be taken into account: namely, the combining or saturating power of the compound, if it is acid or basic; the number of atoms of any one of its elements (generally hydrogen) which may be replaced by other elements; the law of even numbers, which requires that the sum of the numbers of atoms of all the perissad elements (hydrogen, nitrogen, chlorine, &c.) contained in the compound shall be divisible by 2; and the vapor-density of the compound (if it be volatile without decomposition) which, in normally constituted compounds, is always half the molecular weight (p. 229).

The molecular formula may either coincide with the empirical formula, or it may be a multiple of the latter. Thus, the composition of *acetic acid* is expressed by the formula CH_2O, which exhibits the simplest relations of the three elements; but if we want to express the quantities of these, in atoms, required to make up a molecule of acetic acid, we have to adopt the formula $C_2H_4O_2$: for only one-fourth of the hydrogen in this acid is replaceable by metals to form salts, $C_2H_3KO_2$, for example; and its vapor-density, compared with hydrogen, is nearly 30, which is half the weight of the molecule, $C_2H_4O_2 = 2.12 + 4.1 + 2.16$. Again, the empirical formula of benzene is CH; but this contains an uneven number of hydrogen atoms;

and, moreover, if it expressed the weight of the molecule of benzene, the vapor-density of that compound should be $\frac{12+1}{2} = 6{\cdot}5$, whereas experiment shows that it is six times as great, or equal to 39: hence the molecular formula of benzene is C_6H_6.

The deduction of an empirical formula from the ultimate analysis is very easy; the case of sugar, already cited, may be taken as an example. This substance contains, according to the analysis, in 100 parts —

Carbon	41·98
Hydrogen	6·43
Oxygen	51·59
	100·00

If each of these quantities be divided by the atomic weight of the corresponding element, the quotients will express the relations existing between the numbers of atoms of the three elements: these are afterwards reduced to their simplest expression. This is the only part of the calculation attended with any difficulty. If the numbers were rigidly correct, it would only be necessary to divide each by the greatest divisor common to the whole; as they are, however, only approximative, something is of necessity left to the judgment of the experimenter.

In the case of sugar, we have

$$\frac{41{\cdot}98}{12} = 3{\cdot}50; \qquad \frac{6{\cdot}43}{1} = 6{\cdot}43; \qquad \frac{51{\cdot}59}{16} = 3{\cdot}22,$$

or 350 atoms carbon, 643 atoms hydrogen, and 322 atoms oxygen. Now it is evident, in the first place, that the hydrogen and oxygen are present in the proportions to form water, or twice as many atoms of the former as of the latter. Again, the atoms of carbon and hydrogen are nearly in the proportion of 12 : 22, so that the formula $C_{12}H_{22}O_{11}$ appears likely to be correct. It is now easy to see how far this is admissible, by reckoning it back to 100 parts, comparing the result with the numbers given by the actual analysis, and observing whether the difference falls fairly, in direction and amount, within the limits of error of what may be termed a good experiment, viz., two or three-tenths per cent. *deficiency* in the carbon, and not more than one-tenth or two-tenths per cent. *excess* in the hydrogen:

Carbon	$12 \times 12 =$	144
Hydrogen	$1 \times 22 =$	22
Oxygen	$16 \times 11 =$	176
		342

342 : 144 = 100 : 42·11
342 : 222 = 100 : 6·43
342 : 176 = 100 : 51·46

Organic acids and salt-radicals have their molecular weights most frequently determined by an analysis of their lead and silver salts, by burning these latter with suitable precautions in a thin porcelain capsule, and noting the weight of the lead oxide or metallic silver left behind. If the lead oxide be mixed with globules of reduced metal, the quantity of the latter must be ascertained by dissolving away the oxide with acetic acid. Or the lead salt may be converted into sulphate, and the silver compound into chloride, and both metals thus estimated. An organic base, on the contrary, has its

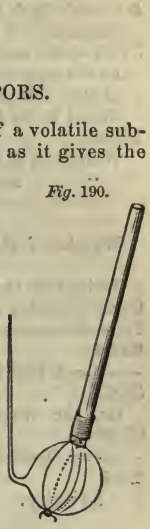
molecular weight fixed by the observation of the quantity of a mineral acid, or an inorganic salt-radical, required to form with it a combination having the characters of neutrality.

The rational and constitutional formulæ of organic compounds will be considered further on.

DETERMINATION OF THE DENSITY OF VAPORS.

The determination of the specific gravity of the vapor of a volatile substance is frequently a point of great importance, inasmuch as it gives the means, in conjunction with the analysis, of representing the constitution of the substance by measure in a gaseous state. The following is a sketch of the plan of operation usually followed: — A light glass globe about three inches in diameter is taken, and its neck softened and drawn out in the blowpipe-flame, as represented in fig. 190: this is accurately weighed. About one hundred grains of the volatile liquid are then introduced, by gently warming the globe and dipping the point into the liquid, which is then forced upwards by the pressure of the air as the vessel cools. The globe is next firmly attached by wire to a handle, in such a manner that it may be plunged into a bath of boiling water or heated oil, and steadily held with the point projecting upwards. The bath must have a temperature considerably above that of the boiling point of the liquid. The latter becomes rapidly converted into vapor, which escapes by the narrow orifice, chasing before it the air of the globe. When the issue of vapor has wholly ceased, and the temperature of the bath, carefully observed, appears pretty uniform, the open extremity of the point is hermetically sealed by a small blowpipe-flame. The globe is removed from the bath, suffered to cool, cleansed if necessary, and weighed, after which the neck is broken off beneath the surface of water which has been boiled and cooled out of contact of air, or (better) of mercury. The liquid enters the globe, and, if the expulsion of the air by the vapor has been complete, fills it; if otherwise, an air-bubble is left whose volume can be easily ascertained by pouring the liquid from the globe into a graduated jar, and then refilling the globe, and repeating the same observation. The capacity of the vessel is thus at the same time known: and these are all the data required.* An example will render the whole intelligible.

Fig. 190.



Determination of the Vapor-Density of Acetone.

Capacity of globe	31·61 cubic inches.
Weight of globe filled with dry air at 52° F. and 30·24 inches barometer	2070·88 grains.
Weight of globe filled with vapor at 212° F. temp. of the bath at the moment of sealing the point, and 30·24 inches barometer	2076·81 grains.
Residual air, at 45° F., and 30·24 inches barometer	0·60 cubic inches.

* Messrs. Playfair and Wanklyn have lately described an important modification of this process, whereby the densities of a vapor at temperatures below the boiling point of the liquid may be determined. This object is attained by mixing the vapor of the body with a measured volume of a permanent gas — hydrogen, for instance. — *Journ. of the Chem. Soc.*, vol. xv. p. 143.

31·61 cubic inches of air at 52° and 30·24 in. bar. = 32·36 cubic inches at 60° F., and 30 inch bar., weighing . . . . . 10·035 grains.
Hence, weight of empty globe, 2070·88 — 10·035 = 2060·845 grains.

0·6 cubic inch of air at 45° = 0·8 cubic inch at 212°; weight of do. by calculation = 0·191 grain.
31·61 — 0·8 = 30·81 cubic inches of vapor at 212° and 30·24 in. bar., which, *on the supposition that it would bear cooling to* 60° *without liquefaction*, would, at that temperature, and under a pressure of 30 inch. bar., become reduced to 24·18 cubic inches.
Hence,

Weight of globe and vapor	2076·810	grains.
" residual air	0·191	
	2076·619	"
Weight of globe	2060·845	"
Weight of the 24·18 cubic inches of vapor . . .	15·774	"
Consequently, 100 cubic inches of such vapor must weigh	65·23	"
100 cubic inches of air, under similar circumstances, weigh	31·01	"

$\frac{65{\cdot}23}{31{\cdot}01} = 2{\cdot}103$, the specific gravity of the vapor in question, air being unity.

Or, the weight of 100 cubic inches of hydrogen being 2·14 grains, $\frac{65{\cdot}23}{2{\cdot}14} = 30{\cdot}44$ is the specific gravity of acetone vapor referred to hydrogen as unity.

In the foregoing statement, we have, for the sake of simplicity, omitted a correction, which, in very exact experiments, must not be lost sight of, viz., the expansion and change of capacity of the glass globe by the elevated temperature of the bath. The density so obtained will be always on this account a little too high.

The error of the mercurial thermometer at high temperatures is in the opposite direction.

The preceding method, which is that of Dumas, is applicable to the determination of the vapor-densities of all substances whose boiling points are within the range of the mercurial thermometer, that is to say, not exceeding 300° C. (572° F.), and therefore to nearly all volatile organic compounds: indeed, there are but few such compounds which can bear higher temperatures without decomposition. But for mineral substances, such as sulphur, iodine, volatile metallic chlorides, &c., it is often necessary to employ much higher temperatures; and for such cases a modification of the process has been devised by Deville and Troost. It consists in using a globe of porcelain instead of glass, heating it in the vapor of a substance whose boiling point is known and constant, and sealing the globe by the flame of the oxy-hydrogen blowpipe. The vapors employed for this purpose are those of mercury, which boils at 350° C. (662° F.); of sulphur, which boils at 440° C. (824° F.); of cadmium, boiling at 860° C. (1580° F.); of zinc, boiling at 1040° C. (1900° F.). The use of these liquids of constant boiling point obviates the necessity of determining the temperature in each experiment, which at such degrees of heat would be very difficult.

In the processes above described, the density of a vapor is determined by weighing the quantity of the vapor contained in a vessel of known ca-

pacity. Another method, devised by Gay-Lussac, consists in ascertaining the volume occupied by a given weight of substance when heated up to a temperature considerably above its boiling point.

The density of a vapor referred to air as unity may be converted into that which it has compared with hydrogen, by dividing by 0·06926, the specific gravity of hydrogen referred to air as unity.

The vapor-density of a compound thus determined, that is to say, the weight of a unit-volume of its vapor compared with that of hydrogen, is found to be in nearly all cases half its molecular weight; for example, the molecular weight of acetone, C_3H_6O, is $36 + 6 + 16 = 58$, the half of which is 29, or nearly equal to the vapor-density of acetone determined by experiment. Hence the law already stated (p. 229), that the molecules of all normally constituted compounds in the state of vapor occupy twice the volume of an atom of hydrogen.

Some compounds, however, exhibit a departure from this rule, their observed specific gravities being equal to only one-fourth their molecular weights, or their molecules occupying four times the volume of an atom of hydrogen. Such is the case with sal-ammoniac, NH_4Cl, phosphorus pentachloride, PCl_5, sulphuric acid, SO_4H_2, ammonium-sulph-hydrate, $SH(NH_4)$, and a few others. This anomaly is probably due, in some cases at least, to a decomposition or "dissociation" of the compound at the high temperature to which it is subjected for the determination of its vapor-density; NH_4Cl, for example, splitting up into NH_3 and HCl, each of which occupies two volumes, and the whole therefore four volumes; and in like manner SO_4H_2 may be supposed to separate into SO_3 and OH_2; PCl_5 into PCl_3 and Cl_2; $SH(NH_4)$ into SH_2 and NH_3, &c.

On the other hand, some substances, both simple and compound, exhibit, at temperatures not far above their boiling points, vapor-densities considerably greater than they should have according to the general law, whereas when raised to higher temperatures they exhibit normal vapor-densities. Thus sulphur, which boils at 440° C. (824° F.), exhibits at 1000° C. (1832° F.), like elementary gases in general, a vapor-density equal to its atomic weight, viz., 32 (see p. 229); but at 500° C. (932° F.) its vapor-density is nearly three times as great. Again, acetic acid, $C_2H_4O_2$, whose molecular weight is $24 + 4 + 16 = 60$, has, at temperatures considerably above its boiling point, a vapor-density nearly equal to 30; but at 125° C. (257° F.), 8° C. (14° F.) above its boiling point, its vapor-density is rather more than 45, or 1½ times as great. This anomalous increase of vapor-density appears to take place when the substance approaches its liquefying point, at which also it exhibits irregularities in its rate of expansion and contraction by variations of pressure and temperature — at which, in short, it begins to behave itself like a liquid; but at higher temperatures it exhibits the physical characters of a perfect gas, and then also its specific gravity becomes normal.

There are two elements, however, namely, phosphorus and arsenic, which, at all temperatures hitherto attained, exhibit a vapor-density twice as great as they should have according to the general law, that of phosphorus being always 62, and that of arsenic 150. This has been explained by supposing that the molecule of each of these elements in the free state contains 4 atoms instead of two, as is the case with most elementary bodies; thus the molecule of phosphorus is supposed to be represented by the formula

DECOMPOSITIONS AND TRANSFORMATIONS OF ORGANIC COMPOUNDS.

Organic bodies are, generally speaking, distinguished by the facility with which they decompose under the influence of heat or of chemical reagents: the more complex the body, the more easily does it undergo decomposition or transformation.

1. *Action of Heat.* — Organic bodies of simple constitution and of some permanence, but not capable of subliming unchanged, like many of the organic acids, yield, when exposed to a high, but regulated temperature, in a retort, new compounds, perfectly definite and often crystallizable, which partake, to a certain extent, of the properties of the original substance: the numerous *pyro-acids*, of which many examples will occur in the succeeding pages, are thus produced. Carbon dioxide and water are often eliminated under these circumstances. If the heat be suddenly raised to redness, the regularity of the decomposition vanishes, while the products become more uncertain and more numerous; carbon dioxide and watery vapor are succeeded by inflammable gases, as carbon monoxide and hydrocarbons; oily matter and tar distil over, and increase in quantity until the close of the operation, when the retort is found to contain, in most cases, a residue of charcoal. Such is *dry* or *destructive distillation.*

If the organic substance contains nitrogen, and is not of a kind capable of taking a new and permanent form at a moderate degree of heat, then that nitrogen is in most instances partly disengaged in the shape of ammonia, or substances analogous to it, partly left in combination with the carbonaceous matter in the distillatory vessel. The products of dry distillation thus become still more complicated.

A much greater degree of regularity is observed in the effects of heat on fixed organic matters, when these are previously mixed with an excess of strong alkaline base, as potash or lime. In such cases an acid, the nature of which is chiefly dependent upon the temperature applied, is produced, and remains in union with the base, the residual element or elements escaping in some volatile form. Thus benzoic acid distilled with calcium hydrate, at a dull red heat, yields calcium carbonate and benzene; woody fibre and caustic potash, heated to a very moderate temperature, yield free hydrogen, and a brown, somewhat indefinite substance called *ulmic acid;* with a higher degree of heat, oxalic acid appears in the place of the ulmic; and, at the temperature of ignition, carbon dioxide, hydrogen being the other product.

2. *Action of Oxygen.*—Oxygen, either free or in the nascent state, in which latter condition it is most active, may act on organic compounds in four different ways:

a. By simple addition, as

$$\underset{\text{Aldehyde.}}{C_2H_4O} + O = \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

β. By simply removing hydrogen:

$$\underset{\text{Alcohol.}}{C_2H_6O} + O = OH_2 + \underset{\text{Aldehyde.}}{C_2H_4O}$$

γ. By removing hydrogen and taking its place, 2 atoms of hydrogen being replaced by one of oxygen; *e. g.:*

$$\underset{\text{Alcohol.}}{C_2H_6O} + O_2 = OH_2 + \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

δ. By removing both carbon and hydrogen. In this manner complex organic bodies containing large numbers of carbon and hydrogen atoms are reduced to others of simpler constitution, and ultimately the carbon and hydrogen are wholly converted into carbon dioxide and water. Nitrogen, chlorine, bromine, and iodine, if present, are at the same time disengaged, for the most part in the free state, and sulphur is oxidized.

Moist organic substances, especially those containing nitrogen, undergo, when exposed to the air, a slow process of oxidation, by which the organic matter is gradually burned and destroyed without sensible elevation of temperature; this process is called *Decay*, or *Eremacausis*. Closely connected with this change are those called *Fermentation* and *Putrefaction*, consisting in a new arrangement of the elements of the compound (often with assimilation of the elements of water), and the consequent formation of new products. The change is called *putrefaction*, when it is accompanied by an offensive odor; *fermentation*, when no such odor is evolved, and especially if the change results in the formation of useful products: thus, the decomposition of a dead body, or of blood or urine, is putrefaction; that of grape-juice or malt-wort, which yields alcohol, is fermentation. Putrefaction and fermentation are not processes of oxidation; nevertheless, the presence of oxygen appears to be indispensable to their commencement; but the change, when once begun, proceeds without the aid of any other substance external to the decomposing body, unless it be water or its elements. Every case of putrefaction thus begins with decay; and if the decay, or its cause, namely, the absorption of oxygen, be prevented, no putrefaction occurs. The most putrescible substances, as animal flesh intended for food, milk, and highly azotized vegetables, are preserved indefinitely, by enclosure in metallic cases from which the air has been *completely* removed and excluded.

Fermentation and putrefaction are always accompanied by the development of certain living organisms of the fungous class; but whether the growth of these is a cause or a consequence of the chemical change is a point not yet decided. We shall return to this subject in speaking of the fermentation of sugar.

3. *Action of Chlorine, Bromine, and Iodine.*—Chlorine and bromine exert precisely similar actions on organic bodies; that of chlorine is the more energetic of the two. The reactions consist:

α. In simple addition of chlorine or bromine to the organic molecule; *e.g.:*

$$\underset{\text{Fumaric acid.}}{C_4H_4O_4} + Br_2 = \underset{\text{Dibromosuccinic acid.}}{C_4H_4Br_2O_4}$$

β. In removal of hydrogen without substitution:

$$\underset{\text{Alcohol.}}{C_2H_6O} + Cl_2 = 2HCl + \underset{\text{Aldehyde.}}{C_2H_4O}$$

γ. In substitution of chlorine or bromine for hydrogen:

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + Cl_2 = HCl + \underset{\text{Chloracetic acid.}}{C_2H_3ClO_2}$$

$$\underset{\text{Acetic acid.}}{C_2H_4O_2} + 3Cl_2 = 3HCl + \underset{\text{Trichloracetic acid}}{C_2HCl_3O_2}$$

The substitution-products thus formed undergo transformations closely analogous to those of the original compounds, under the influence of similar reagents; but they are always more acid, or less basylous, in propor-

tion to the quantity of chlorine or bromine substituted for hydrogen. Thus aniline, C_6H_7N, which is a strong base, may be converted, by processes to be hereafter described, into the chlorinated compounds, C_6H_6ClN, $C_6H_5Cl_2N$, and $C_6H_4Cl_3N$, the first and second of which are less basic than aniline itself, while the third does not show any tendency to form salts with acids.

δ. In presence of water they remove the hydrogen of that liquid, and set free the oxygen: hence, chlorine-water and bromine-water act as powerful oxidizing agents.

Iodine may also act in this manner as an oxidizing agent; and it sometimes attaches itself directly to organic molecules; but it never acts directly by substitution. Iodine substitution-products may, however, be obtained in some cases by treating organic bodies with chloride of iodine, the chlorine then removing hydrogen, and the iodine taking its place.

4. *Action of Nitric Acid.* — This acid acts very powerfully on organic substances. The action may be of three kinds:

α. Direct combination, as with organic bases; *e. g.:*

C_2H_7N	+	NO_3H	=	$C_2H_7N.NO_3H$
Ethylamine.		Nitric acid.		Ethylamine nitrate.

β. Oxidation. This mode of action is most frequently observed with the somewhat diluted acid.

γ. Substitution of nitryl (NO_2) for hydrogen; *e. g.:*

C_6H_6	+	$NO_2(OH)$	=	OH_2	+	$C_6H_5(NO_2)$
Benzene.		Nitric acid.				Nitrobenzene.

$C_6H_{10}O_5$	+	$3NO_2(OH)$	=	$3OH_2$	+	$C_6H_7(NO_2)_3O_5$
Cellulose.		Nitric acid.				Tritrocellulose (gun-cotton).

This action takes place most readily with the strongest nitric acid (pure hydrogen nitrate). The products (called *nitro-compounds*) are always easily combustible, and in many cases highly explosive.

5. *Action of Alkalies.* — The hydrates of potassium and sodium act on organic bodies in a great variety of ways, the most important and general of which are the following: —

α. By direct combination:

CO	+	OKH	=	$CHKO_2$
Carbon monoxide.		Potassium hydrate.		Potassium formate.

$C_{10}H_{16}O$	+	OKH	=	$C_{10}H_{17}KO_2$
Camphor.		Potassium hydrate.		Potassium campholate.

β. By double decomposition with acids, water being eliminated, and a salt produced:

$C_2H_3O_2.H$	+	OKH	=	OH_2	+	$C_2H_3O_2.K$
Acetic acid.						Potassium acetate.

γ. Oxidation, with elimination of hydrogen:

C_2H_6O	+	OKH	=	$C_2H_3KO_2$	+	$2H_2$
Alcohol.				Potassium acetate.		

δ. From chlorinated compounds they remove a part or the whole of the chlorine:

$$\underset{\text{Ethene chloride.}}{C_2H_4Cl_2} + OKH = \underset{\text{Chlor-ethene.}}{C_2H_3Cl} + KCl + OH_2$$

$$\underset{\text{Amyl chloride.}}{C_5H_{11}Cl} + OKH = \underset{\text{Amylene.}}{C_5H_{10}} + KCl + OH_2$$

ε. Amides (pp. 315, 471) are decomposed by them in such a manner that the whole of the nitrogen is given off as ammonia, and a potassium or sodium salt of the corresponding acid is produced:

$$\underset{\text{Acetamide.}}{NH_2 . C_2H_3O} + OKH = NH_3 + \underset{\text{Potassium acetate.}}{C_2H_3O . OK}$$

Many other azotized organic compounds, when heated with alkaline hydrates, likewise give up the whole of their hydrogen in the form of ammonia.

6. *Action of Reducing Agents.* — This name is given to bodies whose action is the inverse of that of oxygen, chlorine, bromine, and iodine; such are nascent hydrogen, obtained by the action of sodium-amalgam on water, or by that of zinc on aqueous acids or alkalies; also hydrogen sulphide, ammonium sulphide, sulphurous acid, and metals, especially potassium and sodium, all of which either give up hydrogen, or abstract oxygen, chlorine, &c.

Reducing agents may act in the following ways: —

α. By adding hydrogen to an organic body:

$$\underset{\text{Ethene oxide.}}{C_2H_4O} + HH = \underset{\text{Alcohol.}}{C_2H_6O}$$

β. By removing oxygen, chlorine, bromine, or iodine, without introducing anything in its place; thus:

$$\underset{\text{Benzoic acid.}}{C_7H_6O_2} + HH = OH_2 + \underset{\text{Benzoic aldehyde.}}{C_7H_6O}$$

γ. By substituting hydrogen for oxygen, chlorine, &c. This process is called *inverse substitution.* It may take place either in equivalent quantities; *e. g.:*

$$\underset{\text{Benzoic acid}}{C_7H_5O . OH} + 2HH = OH_2 + \underset{\text{Benzylic alcohol}}{C_7H_7 . OH}$$

or it may happen that the quantity of hydrogen introduced is only half that which is equivalent to the oxygen removed. This mode of substitution takes place with nitro-compounds, which are thereby reduced to others containing amidogen, (NH_2), in place of nitryl, (NO_2); thus:

$$\underset{\text{Nitrobenzene.}}{C_6H_5(NO_2)} + 3H_2 = 2OH_2 + \underset{\text{Amidobenzene (aniline).}}{C_6H_5(NH_2)}$$

A large number of organic bases are formed in this manner from nitro-compounds.

7. *Action of Dehydrating Agents.* — Strong sulphuric acid, sulphuric oxide, phosphoric oxide, and zinc chloride remove oxygen and hydrogen from organic bodies in the form of water, the elements of which are derived,

sometimes from a single molecule of the organic body, sometimes from two molecules:

$$\underset{\text{Alcohol.}}{C_2H_6O} - OH_2 = \underset{\text{Ethene.}}{C_2H_4}$$

$$\underset{\text{Alcohol.}}{2C_2H_6O} - OH_2 = \underset{\text{Ether.}}{C_4H_{10}O}$$

Compounds which, like sugar, starch, and woody fibre, consist of carbon united with hydrogen and oxygen in the proportions to form water, are often reduced by these dehydrating agents to black substances consisting mainly of carbon.

Other reactions of less generality than those above described will be sufficiently illustrated by special cases in the sequel.

CLASSIFICATION OF ORGANIC COMPOUNDS.—ORGANIC SERIES.

The classification of organic compounds is based upon the equivalence or atomicity of carbon. This element is a tetrad, being capable of uniting with at most four atoms of hydrogen or other monatomic elements. Methane or marsh gas, CH_4, is therefore a saturated hydro-carbon, not capable of uniting directly with chlorine, bromine, or other monad elements, but only of exchanging a part or the whole of its hydrogen for an equivalent quantity of another monad element. It may, however, as already explained (p. 235), take up any number of dyad elements or radicals, because such a radical introduced into any group of atoms whatever, neutralizes one unit of equivalency, and adds another, leaving therefore the combining power or equivalence of the group just the same as before. Accordingly, the hydro-carbon, CH_4, may take up any number of molecules of the bivalent radical, CH_2, thereby giving rise to the series of saturated hydro-carbons,

$$CH_4, \quad C_2H_6, \quad C_3H_8, \quad C_4H_{10} \ldots . \; C\,H_{2n+2}.*$$

A series of compounds, the terms of which differ from one another by CH_2, is called an *homologous series*. There are many such series besides that of the hydro-carbons just mentioned; thus methyl-chloride, CH_3Cl, gives by continued addition of CH_2, the series of chlorides,

$$CH_3Cl, \quad C_2H_5Cl, \quad C_3H_7Cl, \quad C_4H_9Cl \ldots C\,H_{2n+}\,Cl;$$

and from methyl-alcohol, CH_4O, is derived in like manner the series of homologous alcohols,

$$CH_4O, \quad C_2H_6O, \quad C_3H_8O, \quad C_4H_{10}O \ldots C_n\,H_{2n+}\,O.$$

The terms of the same homologous series resemble one another in many respects, exhibiting similar transformations under the action of given reagents, and a regular gradation of properties from the lowest to the highest; thus, of the hydro-carbons, $C_n\,H_{2n+2}$, the lowest terms CH_4, C_2H_6, and C_3H_8, are gaseous at ordinary temperatures, the highest containing 20 or more carbon-atoms, are solid, while the intermediate compounds are liquids, becoming more and more viscid and less volatile, as they contain a greater number of carbon-atoms, and exhibiting a constant rise of about 20° C. (36° F.) in their boiling points for each addition of CH_2 to the molecule.

The saturated hydro-carbons, $C_n\,H_{2n+2}$, may, under various circumstances,

* See page 234.

be deprived of two atoms, or one molecule, of hydrogen, thereby producing a new homologous series,

$$CH_2, \quad C_2H_4, \quad C_3H_6, \quad C_4H_8 \ldots C_nH_{2n}.$$

These are unsaturated molecules, having two units of equivalency uncombined, and therefore acting as bivalent radicals, capable of taking up 2 atoms of chlorine, bromine, or other univalent radicals, and 1 atom of oxygen or other bivalent radical.

The first term of this last series cannot give up 2 atoms of hydrogen without being reduced to the atom of carbon; but the remaining terms may each give up 2 atoms of hydrogen, and thus give rise to the series,

$$C_2H_2, \quad C_3H_4, \quad C_4H_6 \ldots C_nH_{2n-2}.$$

each term of which is a quadrivalent radical.

And, in like manner, by successive abstractions of H_2, a number of homologous series may be formed whose general terms are

$$C_nH_{2n+2}, \quad C_nH^{2n}, \quad C_nH_{2n-2}, \quad C_nH_{2n-4} \ldots \text{ \&c.}$$

The individual series, as far as C_6, are given in the following table, together with the names proposed for them by Dr. Hofmann:*

CH_4	CH_2				
Methane	Methene				
C_2H_6	C_2H_4	C_2H_2			
Ethane	Ethene	Ethine			
C_3H_8	C_3H_6	C_3H_4	C_3H_2		
Propane	Propene	Propine	Propone		
C_4H_{10}	C_4H_8	C_4H_6	C_4H_4	C_4H_2	
Quartane	Quartene	Quartine	Quartone	Quartune	
C_5H_{12}	C_5H_{10}	C_5H_8	C_5H_6	C_5H_4	C_5H_2
Quintane	Quintene	Quintine	Quintone	Quintune	
C_6H_{14}	C_6H_{12}	C_6H_{10}	C_6H_8	C_6H_6	C_6H_4 $\quad C_6H_2$.
Sextane	Sextene	Sextine	Sextone	Sextune	

Each vertical column of this table forms a homologous series, in which the terms differ by CH_2, and each horizontal line an *isologous series*, in which the successive terms differ by H_2. The bodies of these last series are designated as the monocarbon, dicarbon group, &c.

The formulæ in the preceding table represent hydrocarbons all of which are capable of existing in the separate state, and many of which have been actually obtained. They are all derived from saturated molecules, C_nH_{2n+2}, by abstraction of one or more *pairs* of hydrogen-atoms.

But a saturated hydrocarbon, CH_4, for example, may give up 1, 2, 3, or any number of hydrogen-atoms in exchange for other elements; thus marsh gas, CH_4, subjected to the action of chlorine under various circumstances, yields the substitution-products,

$$CH_3Cl, \quad CH_2Cl_2, \quad CHCl_3, \quad CCl_4,$$

which may be regarded as compounds of chlorine with the radicals,

$$(CH_3)', \quad (CH_2)'', \quad (CH_3)''', \quad C^{iv};$$

and in like manner each hydrocarbon of the series, C_nH_{2n+2}, may yield a series of radicals of the forms,

$$(C_nH_{2n+1})', \quad (C_nH_{2n})'', \quad (C_nH_{2n-1})''', \quad (C_nH_{2n-2})^{iv}, \text{ \&c.}$$

each of which has an equivalent value, or combining power, corresponding

* Proceedings of the Royal Society, xv. 57.

with the number of hydrogen-atoms abstracted from the original hydrocarbon. Those of even equivalence contain even numbers of hydrogen-atoms, and are identical in composition with those in the table above given; but those of uneven equivalence contain odd numbers of hydrogen-atoms, and are incapable of existing in the separate state, except, perhaps, as double molecules (p. 238).

These hydrocarbon radicals of uneven equivalence are designated by names ending in *yl*, those of the univalent radicals being formed from methane, ethene, &c., by changing the termination *ane* into *yl;* those of the trivalent radicals by changing the final *e* in the names of the bivalent radicals, methene, &c., into *yl;* and similarly for the rest. The names of the whole series will therefore be as follows: —

CH_4	$(CH_3)'$	$(CH_2)''$	$(CH)'''$			
Methane	Methyl	Methene	Methenyl			
C_2H_6	$(C_2H_5)'$	$(C_2H_4)''$	$(C_2H_3)'''$	$(C_2H_2)^{iv}$	$(C_2H)^{v}$	
Ethane	Ethyl	Ethene	Ethenyl	Ethine	Ethinyl	
C_3H_8	$(C_3H_7)'$	$(C_3H_6)''$	$(C_3H_5)'''$	$(C_3H_4)^{iv}$	$(C_3H_3)^{v}$	$(C_3H_2)^{vi}$ $(C_3H)^{vii}$
Propane	Propyl	Propene	Propenyl	Propine	Propinyl	Propone Proponyl.
		&c.		&c.		&c.

From these hydrocarbon radicals, others of the same degree of equivalence may be derived by partial or total replacement of the hydrogen by other elements, or compound radicals. Thus from propyl, C_3H_7, may be derived the following univalent radicals: —

C_3H_6Cl	$C_3H_3Cl_4$	C_3H_5O	$C_3H_2Cl_3O$	$C_3H_6(CN)'$
Chloropropyl	Tetrachloro-propyl	Oxypropyl	Trichlor-oxypropyl	Cyanopropyl.
$C_3H_6(NO_2)$	$C_3H_4(NH_2)O$	$C_3H_6(CH_3)$	$C_3H_5(C_2H_5)_2$	
Nitropropyl.	Amidoxypropyl	Methylpropyl	Diethylpropyl.	

From the radicals above mentioned, all well-defined organic compounds may be supposed to be formed by combination and substitution, each radical entering into combination, just like an elementary body of the same degree of equivalence.

Organic compounds may thus be arranged in the following classes:

I. *Hydrocarbons containing even numbers of hydrogen atoms.*—These are the compounds tabulated on page 467; they are sometimes regarded as hydrides of radicals containing uneven numbers of hydrogen atoms; *e. g.*:

Methane, $CH_4 = CH_3 . H$, Methyl hydride.

II. *Haloïd Ethers.*—Compounds of hydrocarbons with halogens; *e. g.*:

CH_3Cl	$C_2H_4Br_2$	$C_3H_5I_3$
Methyl chloride.	Ethene bromide.	Propenyl iodide.

These compounds are often formed by direct substitution of chlorine, bromine, &c., for hydrogen in hydrocarbons containing even numbers of hydrogen atoms.

III. *Alcohols.* — Compounds of hydrocarbon radicals (hence called *alcohol radicals*), with hydroxyl; *e. g.*:

$C_2H_5(HO)$	$(C_2H_4)''(HO)_2$	$(C_3H_5)'''(HO)_3$
Ethyl alcohol.	Ethene alcohol (Glycol).	Propenyl alcohol (Glycerin).

These compounds may be formed from the corresponding haloïd ethers, by the action of water or alkalies, just as metallic hydrates are formed from the corresponding chlorides, &c.

IV. *Oxygen Ethers*, or *Alcoholic Oxides.* — Compounds of hydrocarbon radicals with oxygen; *e. g.:*

$(C_2H_5)_2O$	$(C_2H_4)''O$	$(C_3H_5)'''_2O_3$
Ethyl oxide.	Ethene oxide.	Propenyl oxide.

These ethers are related to the alcohols in the same manner as anhydrous metallic oxides to the corresponding hydrates or hydrylates, and may be formed, in many instances, by direct dehydration of the alcohols, as by the action of sulphuric acid, zinc chloride, &c.

V. *Sulphur* and *Selenium Alcohols* and *Ethers.* — Compounds analogous in composition to the oxygen alcohols and ethers, the oxygen being replaced by sulphur or selenium. The sulphur and selenium alcohols are also called mercaptans.

VI. *Acid Halides.* — Compounds of oxygenated radicals (acid radicals) with chlorine, bromine, &c.; *e. g.:*

$C_2H_3O.Cl$	$(C_4H_4O_2)''Cl_2$	$(C_6H_5O)_4'''Cl_3$
Acetyl chloride.	Succinyl chloride.	Citryl chloride.

These compounds are formed by the action of the chlorides, bromides, &c., of phosphorus on the compounds of the next class.

VII. *Organic Acids.* — Compounds of oxygenated radicals with hydroxyl; *e. g.:*

$C_2H_3O.HO$	$(C_4H_4O_2)''.(HO)_2$	$(C_6H_5O_4)'''.(HO)_3$
Acetic acid.	Succinic acid.	Citric acid.

These compounds are formed in a variety of ways; among others, by oxidation of alcohols, and by the action of water on the corresponding acid halides, just as alcohols are formed from alcoholic chlorides. A very large number of them exist also ready-formed in the bodies of plants and animals.

The hydrogen in the radicals of these acids may be more or less replaced by chlorine, bromine, nitryl, (NO_2), and other chlorous radicals; thus, from benzoic acid, $C_7H_5.HO$, are derived:

$C_7H_4ClO.HO$	$C_7H_5(NO_2)O.HO$	$C_7H_5(NH_2)O.HO$
Chlorobenzoic acid.	Nitrobenzoic acid.	Amidobenzoic acid.

VIII. *Acid Oxides*, sometimes called Anhydrous acids, or Anhydrides; *e. g.:*

$(C_2H_3O)_2O$	$(C_2H_4O_2)''O$	$(C_2H_3O)(C_7H_5O)O$
Acetic oxide.	Succinic oxide.	Acetobenzoic oxide.

These are related to the acids in the same manner as the oxygen-ethers to the alcohols, and are formed from them in some instances by direct dehydration.

IX. *Ethereal Salts*, also called *Compound Ethers.* — Compounds formed from acids by substitution of alcohol radicals for hydrogen, just as metallic salts are produced by substitution of metals for the hydrogen in acids; *e. g.:*

$C_2H_3O_2.H$	$SO_4.HH$	$PO_4.HHH$
Acetic acid.	Sulphuric acid.	Phosphoric acid.

$C_2H_3O_2 \cdot C_2H_5$ Ethylic acetate.	$SO_4 \cdot (C_2H_5)H$ Monethylic sulphate.	$PO_4 \cdot (C_2H_5)HH$ Monethylic phosphate.
	$SO_4 \cdot (C_2H_5)_2$ Diethylic sulphate.	$PO_4 \cdot (C_2H_5)_2H$ Diethylic phosphate.
		$PO_4 \cdot (C_2H_5)_3$ Triethylic phosphate.

They are produced in many cases by heating an acid or the corresponding chloride with an alcohol.

X. *Aldehydes.* — These are compounds intermediate between alcohols and acids. Thus:

C_2H_6O Ethyl alcohol.	C_2H_4O Acetic aldehyde.	$C_2H_4O_2$ Acetic acid.

They are produced by oxidation of alcohols, and are reconverted into the latter by the action of nascent hydrogen. By further oxidation they are converted into acids.

XI. *Ketones.* — These are bodies derived from aldehydes by the replacement of 1 atom of hydrogen by an alcohol radical; *e.g.:*

Acetic ketone or Acetone, $C_3H_6O = C_2H_3(CH_3)O$.

They are produced by the dry distillation of the calcium or barium salts of monobasic acids, and by other processes which will be mentioned further on.

XII. *Amines,* also called *Alcohol-bases,* or *Compound ammonias.* — Compounds of alcohol radicals with amidogen, $(NH_2)'$, imidogen, $(NH)''$, and trivalent nitrogen; *e.g.:*

$C_2H_5 \cdot H_2N$ Ethylamine.	$(C_2H_5)_2 \cdot HN$ Diethylamine.	$(C_2H_5)_3N$ Triethylamine.
$(C_2H_4)'' \cdot (H_2N)_2$ Ethene-diamine.	$(C_2H_4)''_2 \cdot (HN)_2$ Diethene-diamine.	$(C_2H_4)''_2 \cdot N_2$. Triethene-diamine.

The modes of formation of these bodies will be explained hereafter. They are mostly of basic character, and capable of forming salts with acids, like ammonia, H_3N, from which they may, in fact, be derived by substitution of alcohol radicals for part or the whole of the hydrogen. Those in which the hydrogen is wholly thus replaced are called *nitriles;* and among these special mention must be made of a group consisting of nitrogen combined with a trivalent hydrocarbon radical, such as —

$(CH)'''N$ Methenyl nitrile.	$(C_2H_3)'''N$ Ethenyl nitrile.	$(C_3H_5)'''N$ Propenyl nitrile.

These nitriles have no basic properties, but are all neutral, except the first, which is a monobasic acid, capable of exchanging its hydrogen for metals, and in this character may be regarded as a compound of hydrogen with the univalent radical cyanogen — $C \equiv N$; it is accordingly named *hydrogen cyanide,* or *hydrocyanic acid,* and the other nitriles homologous with it are the ethers of this acid; thus:

Methenyl nitrile, $(CH)'''N = CN.H$, Hydrogen cyanide,
Ethenyl nitrile, $(C_2H_3)'''N = CN.CH_3$, Methyl cyanide,
Propenyl nitrile, $(C_3H_5)'''N = CN.C_2H_5$, Ethyl cyanide.

The metallic cyanides have been already noticed (p. 277).

XIII. *Alcoholic Ammonium-compounds.* — Compounds containing pentad nitrogen, and having the composition of ammonium salts in which the hydrogen is more or less replaced by alcohol radicals; *e.g.:*

$N^{v}(C_2H_5)H_3Cl$ Ethylammonium chloride,
$N^{v}(C_2H_5)_2H_2Cl$ Diethylammonium chloride,
$N^{v}(C_2H_5)_3HCl$ Triethylammonium chloride,
$N^{v}(C_2H_5)_4Cl$ Tetrethylammonium chloride,
$N_{v}(C_2H_5)_4(HO)$ Tetrethylammonium hydrylate.

This last compound and its analogues, containing methyl, amyl, &c., are powerful alkalies, obtainable in the solid state, by evaporation of their aqueous solutions, as white deliquescent crystalline masses resembling caustic potash.

XIV. *Phosphorus*, *Arsenic*, and *Antimony Compounds*, analogous to the nitrogen compounds XII. and XIII.; *e.g.:*

$P'''(CH_3)_3$ Triethyl phosphine.	$As'''(C_2H_5)_3$ Triethyl arsine.	$Sb'''(C_2H_5)_3$ Triethyl stibine.
$P^{v}(CH_3)_4Cl$ Tetramethyl-phosphonium chloride.	$As^{v}(CH_3)(C_2H_5)_3Cl$ Methyl-triethyl-arsonium chloride.	$Sb^{v}(C_2H_5)_4(HO)$ Tetrethyl-stibonium hydrate.

XV. *Organo-metallic bodies*, not analogous to ammonia or ammonium salts. — Compounds of hydrocarbon radicals with monad, dyad, and tetrad metals; *e.g.:*

NaC_2H_5 Sodium ethide.	$Zn''(CH_3)_2$ Zinc ethide.	$Sn^{iv}(C_2H_5)_{iv}$ Stannic ethide.
$Hg''(CH_3)Cl$ Mercuric chloromethide.	$Sn^{iv}(C_2H_5)Cl_3$ Stannic chlorotriethide.	$Sn^{iv}(CH_3)_2I_2$ Stannic dimethyl di-iodide.

XVI. *Amides.* — Compounds exactly analogous to the amines, but with acid radicals instead of alcohol radicals; those which contain bivalent acid radicals combined with imidogen, $(NH)''$, are called imides; *e.g.:*

Acetamide	$C_2H_3O.H_2N$	Succinamide	$(C_4H_4O_2)''.(H_2N)_2$
Diacetamide	$(C_2H_3O)_2.HN$	Trisuccinamide	$(C_4H_4O_2)_3''.N'''_2$
Succinimide	$(C_4H_4O_2)''.HN$	Citramide	$(C_6H_5O_4)'''.N'''.$

XVII. *Amic acids.* — Acids consisting of a bivalent or trivalent acid radical combined with hydroxyl and with amidogen; *e.g.:*

Succinamic acid $(C_4H_4O_2)''.HO.H_2N$
Citramic acid* $(C_6H_5O_4)'''.HO.(HN)''.$

Each of the classes of carbon compounds above enumerated may be divided into homologous and isologous groups, though in most cases the series are far from being complete.

* This compound is not actually known; but its derivative, phenyl-citramic acid, $(C_6H_5O_4)'''.C_6H_5O.HN$, has been obtained.

The preceding classes, most of which have their analogues amongst inorganic compounds, include nearly all artificially prepared organic bodies, and the majority of those produced in the living organism. There are still, however, many compounds formed in the bodies of plants and animals, the chemical relations of which are not yet sufficiently well made out to enable us to classify them with certainty. Such is the case with many vegetable oils and resins, with most of the alkaloïds or basic nitrogenized compounds found in plants, such as morphine, quinine, strychnine, &c., and several definite compounds formed in the animal organism, as albumin, fibrin, casein, and gelatin.

Rational Formulæ of Organic Compounds — It must be distinctly understood that the formulæ above given are not the only ones by which the constitution of the several classes of organic compounds may be represented. Rational formulæ are intended to represent the mode of formation and decomposition of compounds, and the relation which allied compounds bear to one another: hence, if a compound can, under varying circumstances, split up into different atomic groups or radicals, or if it can be formed in various ways by the combination of such radicals, different rational formulæ must be assigned to it. This point has been already noticed in connection with the constitution of metallic salts, and illustrated especially in the case of the sulphates (p. 281); but organic compounds, which for the most part contain larger numbers of atoms, and are therefore capable of division into a greater number of groups, afford much more abundant illustration of the same principle. Take, for example, acetic acid, the molecular formula of which is $C_2H_4O_2$. This may be resolved into the following rational formulæ:

1. $C_2H_3O_2.H$. — This formula, analogous to that of hydrochloric acid, Cl.H, indicates that a molecule of acetic acid can give up one atom of hydrogen in exchange for a univalent metal or alcohol-radical, forming, for example, sodium acetate, $C_2H_3O_2.Na$, ethyl acetate, $C_2H_3O.C_2H_5$, &c.; that two molecules of the acid may give up two hydrogen atoms in exchange for a bivalent metal or alcohol-radical, forming barium acetate, $(C_2H_3O_2)_2Ba''$, ethene acetate, $(C_2H_3O_2)_2.(C_2H_4)''$, &c.; in other words, that acetic acid is a monobasic acid (p. 282).

2. $C_2H_3O.HO$. — This formula, analogous to that of water, H.HO, corresponds to such reactions as the formation of acetic acid from acetic chloride by the action of water:

$$C_2H_3O.Cl + H.HO = HCl + C_2H_3O.HO.$$

3. $C_2H_3O.H.O$. — This formula, also comparable to that of water, HH.O, corresponds to the conversion of acetic acid into acetic chloride, hydrochloric acid, and phosphorus oxychloride, by the action of phosphorus pentachloride:

$$C_2H_3O.H.O + PCl_3.Cl_2 = C_2H_3O.Cl + HCl + PCl_3O;$$

also to the formation of thiacetic acid, $C_2H_3O.H.S$, by the action of phosphorus pentasulphide on acetic acid:

$$5(C_2H_3O.H.O) + P_2S_5 = 5(C_2H_3O.H.S) + P_2O_5.$$

4. $(C_2H_3)'''.HO.O$. — This represents the formation of acetic acid from ethenyl nitrile, $(C_2H_3)'''N$, by heating with caustic alkalies:

$$(C_2H_3)'''N + \left.\begin{matrix}HH.O\\H.HO\end{matrix}\right\} = NH_2 + (C_2H_3)'''.O.HO.$$

Ethenyl nitrile. Water.

5. $(CH_3 . CO) . HO$. — This formula, in which the radical acetyl, C_2H_3O, is resolved into carbonyl, $(CO)''$, and methyl, corresponds: *a*. To the decomposition of acetic acid by electrolysis, in which hydrogen is evolved at the positive pole, while carbon dioxide and ethane, C_2H_6, appear at the negative:

$$2(CO . CH_3 . HO) = H_2 + C_2H_6 + 2CO_2.$$

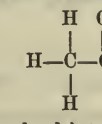
β. To the production of methane (marsh gas) by heating potassium acetate with excess of potassium hydrate (p. 169):

$CO . CH_3 . KO$	+	HKO	=	CH_4	+	$(CO)'' . (KO)_2$.
Potassium acetate.		Potassium hydrate.		Methane.		Potassium carbonate.

γ. To the production of acetone and barium carbonate by the dry distillation of barium acetate:

$(CO . CH_3)_2 . BaO_2$	=	$(CO)''(CH_3)_2$	+	$(CO)'' . BaO_2$.
Barium acetate.		Acetone.		Barium carbonate.

Now, on comparing those several rational formulæ, it will be seen that they are all included under the constitutional formula,



in which the molecule is resolved into its component atoms, and these atoms are grouped, as far as possible, according to their different equivalences, or combining powers. These constitutional formulæ are the nearest approach to the representation of the true constitution of a compound that our knowledge of its reactions enables us to give; but the student cannot too carefully bear in mind that they are not intended to represent the actual arrangement of the atoms in space, but only, as it were, their relative mode of combination, showing which atoms are combined together directly, and which only indirectly, that is, through the medium of others. Thus, in the formula of acetic acid, it is seen that three of the hydrogen atoms are united directly with the carbon, while the fourth is united to it only through the medium of oxygen; that one of the two oxygen atoms is combined with carbon alone, the other both with carbon and with hydrogen; and that one of the carbon atoms is combined with the other carbon atom and with hydrogen; the second with carbon and with oxygen. Abundant illustration of these principles will be afforded by the special descriptions of organic compounds in the following pages.

Isomerism. — Two compounds are said to be isomeric when they have the same empirical formula or percentage composition, but exhibit different properties. A few examples of isomerism are met with amongst inorganic compounds; but they are much more numerous amongst organic or carbon compounds.

Isomeric bodies may be divided into two principal groups, namely:

A. — Those which have the same molecular weight; and these are subdivided into:

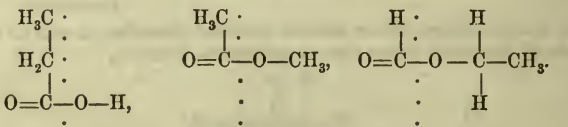
a. *Isomeric bodies*, strictly so called; namely, those which exhibit analogous decompositions and transformations when heated or subjected to the action of the same reagents, and differ only in physical properties. Such is the case with the volatile oils of turpentine, lemons, juniper, &c., all of which have the composition $C_{10}H_{16}$, resemble each other closely in their chemical reactions, and are distinguished chiefly by their odor and their action on polarized light.

β. Metameric bodies, which, with the same percentage composition and molecular weight, exhibit dissimilar transformations under similar circumstances. Thus the molecular formula, $C_3H_6O_2$, represents three different bodies, all exhibiting different modes of decomposition under the influence of caustic alkalies, viz., (1) Propionic acid, C_3H_5O . OH, which is converted by caustic potash, at ordinary temperatures, into potassium propionate, C_3H_5O . OK. — (2) Methyl acetate, C_2H_3O . OCH_3, a neutral liquid not acted upon by potash at common temperatures, but yielding, when heated with it, potassium acetate and methyl alcohol:

$$C_2H_3O \,.\, OCH_3 + OKH = C_2H_3O \,.\, OK + CH_3 \,.\, OH.$$

(3) Ethyl formate, CHO . OC_2H_5, converted in like manner, by heating with potash, into potassium formate, CHO . OK, and ethyl alcohol, C_2H_5.OH.

These three compounds may be represented by the following constitutional formulæ, the dotted lines indicating the division into radicals indicated by the rational formulæ above given:



Propionic acid. Methyl acetate. Ethyl formate.

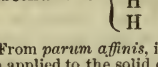
B.—Compounds which have the same percentage composition, but differ in molecular weight; such bodies are called polymeric. The most striking example of polymerism is exhibited by the hydro-carbons C_nH_{2n}, all of which are multiples of the lowest, namely, methene, CH_2. Another example is afforded by certain natural volatile oils, which are polymeric with oil of turpentine, and have the formulæ, $C_{20}H_{32}$, $C_{30}H_{48}$, &c. All polymeric compounds exhibit regular gradations of boiling point, vapor-density, and other physical characters from the lowest to the highest. Some are chemically isomeric, exhibiting analogous transformations under similar circumstances, while others are metameric, exhibiting dissimilar reactions under given circumstances.

HYDROCARBONS.

First Series, C_nH_{2n+2}.—Paraffins.*

This series, as already observed, consists of saturated hydrocarbons, not capable of uniting with any other bodies, simple or compound. The names and formulæ of the first six are given in the table on page 467; the following terms may be called, *septane*, *octane*, *nonane*, *decane*, *undecane*, *dodecane*, &c.

All the members of the series above the first, CH_4, may be regarded as derived from that compound by replacement of one of the hydrogen-atoms, by a univalent hydrocarbon radical of the series C_nH_{2n+1} (p. 466); thus.



* From *parum affinis*, indicating their chemical indifference. The name paraffin has long been applied to the solid compounds of the series, on account of this character; and many of the liquid compounds of the same series are known commercially as *paraffin oils*. It is convenient, therefore, to employ the term paraffin as a generic name for the whole series.

Ethane $C_2H_6 = C\left\{\begin{matrix} CH_3 \\ H_3 \end{matrix}\right.$

Propane $C_3H_8 = C\left\{\begin{matrix} C_2H_5 \\ H_3 \end{matrix}\right. = C\left\{\begin{matrix} CH_2CH_3 \\ H_3 \end{matrix}\right.$

Quartane $C_4H_{10} = C\left\{\begin{matrix} C_3H_7 \\ H_3 \end{matrix}\right. = C\left\{\begin{matrix} CH_2C_2H_5 \\ H_3 \end{matrix}\right. = C\left\{\begin{matrix} CH_2CH_2CH_3 \\ H_3 \end{matrix}\right.$

&c., &c.

Occurrence and Formation.—Many of the paraffins occur ready-formed in American petroleum and other mineral oils of similar origin. They are formed artificially by the following processes:

1. By the simultaneous action of zinc and water on the alcoholic iodides (p. 468), compounds derived from these same hydrocarbons by the substitution of one atom of iodine for hydrogen.

This reaction, which appears to be applicable to the formation of the whole series of paraffins, is represented by the general equation:

$$\underset{\text{Alcoholic iodide.}}{2C_nH_{2n+1}I} + \underset{\text{Zinc.}}{Zn_2} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Zinc hydrate.}}{ZnH_2O_2} + \underset{\text{Zinc iodide.}}{ZnI_2} + \underset{\text{Paraffin.}}{2C_nH_{2n+2}}$$

As an example, we may take the formation of ethane from ethyl iodide:

$$\underset{\text{Ethyl iodide.}}{2C_2H_5I} + Zn_2 + OH_2 = ZnH_2O_2 + ZnI_2 + \underset{\text{Ethane.}}{2C_2H_6}$$

2. All the paraffins may be produced by heating the alcoholic iodides with zinc alone. Generally speaking, however, two of these hydrocarbons are obtained together, the first product of the reaction being a paraffin containing twice as many carbon-atoms as the alcoholic iodide employed; and this compound being then partly resolved into the paraffin containing half this number of carbon-atoms and the corresponding olefine, (C_nH_{2n}); thus:

$$\underset{\text{Ethyl iodide.}}{2C_2H_5I} + Zn = ZnI_2 + \underset{\text{Quartane.}}{C_4H_{10}}$$

and,

$$\underset{\text{Quartane.}}{C_4H_{10}} = \underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Ethane.}}{C_2H_6}$$

Generally:

$$2C_nH_{2n+1}I + Zn = ZnI_2 + C_{2n}H_{4n+2}$$

and,

$$C_{2n}H_{2n+2} = C_nH_{2n} + C_nH_{2n+2}.$$

3. By the electrolysis of the fatty acids ($C_nH_{2n}O_2$). For example, a solution of potassium acetate, divided into two parts by a porous diaphragm, yields pure hydrogen, together with potash, at the negative electrode, and at the positive electrode (if of platinum) a mixture of carbon dioxide and ethane gases:

$$2C_2H_4O_2 = 2CO_2 + C_2H_6 + H_2.$$

We may suppose that the two molecules of acetic acid are resolved by the current into H_2 and $C_4H_6O_4$, and that the latter then splits up into $2CO_2$ and C_2H_6. The general reaction is:

$$2C_nH_{2n}O_2 = 2CO_2 + C_{2n-2}H_{4n-2} + H_2.$$

4. Some of the paraffins are obtained from acids of the series $C_nH_{2n}O_2$

and $C_nH_{2n-2}O_4$, by the action of alkalies, which abstract carbon dioxide from those acids, the hydrocarbon thus eliminated containing one atom of carbon less than the acid from which it is produced:

$$C_{n+1}H_{2n+2}O_2{}^* = CO_2 + C_nH_{2n+2},$$
$$C_{n+2}H_{2n+2}O_4 = 2CO_2 + C_nH_{2n+2}.$$

In this maner methane (marsh gas) is obtained by heating potassium acetate with excess of potassium hydrate (p. 169):

$C_2H_3O_2K$	+	OHK	=	CO_3K_2	+	CH_4
Potassium acetate.		Potassium hydrate.		Potassium carbonate.		Methane.

Also, sextane and octane, by similar treatment of the potassium salts of suberic acid, $C_8H_{14}O_4$, and sebacic acid, $C_{10}H_{18}O_4$:

$C_8H_{12}O_4K_2$	+	2OHK	=	$2CO_3K_2$	+	C_6H_{14}
Potassium suberate.						Sextane.
$C_{10}H_{16}O_4K_2$	+	2OHK	=	$2CO_3K_2$	+	C_8H_{18}
Potassium sebate.						Octane.

Generally speaking, however, a further decomposition takes place, resulting in the formation of hydrocarbons containing a smaller proportion of hydrogen than the paraffins.

5. The paraffins may also be produced from the olefines, C_nH_{2n}, by combining the latter with bromine, and heating the resulting compound, $C_nH_{2n}Br_2$, with a mixture of potassium iodide, water, and metallic copper. The bromine-compound is then decomposed, and the hydrocarbon, C_nH_{2n}, is partly reproduced in the free state, partly converted, by the addition of hydrogen, into a paraffin, C_nH_{2n+2}.

6. Several of the paraffins are produced by the dry or destructive distillation of butyrates and acetates.

7. They are also found amongst the products of the dry distillation of coal, especially Boghead and Cannel coal, and, as already observed, they constitute the principal portion of many mineral oils, formed by the gradual decay or decomposition of vegetable matter beneath the earth's surface.

8. Quintyl alcohol, or amyl alcohol, $C_5H_{12}O$, distilled with zinc chloride, yields quintane, C_5H_{12}, and several of its homologues, together with olefines and other hydrocarbons containing still smaller proportions of hydrogen.

9. Methane, or marsh gas, CH_4, the first term of the series, is produced synthetically by passing a mixture of hydrogen sulphide and vapor of carbon bisulphide over red-hot copper. The copper abstracts the sulphur from both compounds, and the carbon and hydrogen thus liberated unite to form marsh gas:—

$$CS_2 + 2H_2S + Cu_4 = 4CuS + CH_4.$$

Properties and Reactions of the Paraffins.—The properties of methane have been already described (p. 169). Of the other paraffins, ethane, propane, and quartane are gaseous at ordinary temperatures; most of the others are liquids regularly increasing in specific gravity, viscidity, boiling point, and vapor density, as their molecular weight becomes greater: those containing 20 carbon atoms or more are crystalline solids. The following table exhibits the specific gravities and boiling points of the paraffins obtained from American petroleum:†—

* By substitution of $n+1$ for n, the formula $C_nH_{2n}O_2$ becomes $C_{+1}H_{2n+2}O_2$; and by substitution of $n+2$ for n, the formula $C_nH_{2n-2}O_4$ is converted into $C_{+2}H_{2n+2}O_4$.

† Pelouze and Cahours, Ann. Ch. Pharm. cxxiv. 289; cxxvii. 196; cxxix. 87.

Name.	Formula.	Boiling point.	Specific gravity of liquid.	Specific gravity of vapor hydrogen = 1.
Ethane	C_2H_6	Gaseous at ordinary temperatures.	—	15
Propane	C_3H_8	"	—	22
Quartane	C_4H_{10}	a little above 0°	0·60 at 0° C. 32° F.	29
Quintane	C_5H_{12}	30° C. 86° F.	0·628 " 17° " 63° "	36
Sextane	C_6H_{14}	68° " 154° "	0·669 " 16° " 61° "	43
Septane	C_7H_{16}	92—94° " 198—201° "	0·699 " 15° " 59° "	50
Octane	C_8H_{18}	116—118° " 241—245° "	0·726 " 15° " 59° "	57
Nonane	C_9H_{20}	136—138° " 277—280° "	0·741 " 15° " 59° "	64
Decane	$C_{10}H_{22}$	160—162° " 320—324° "	0·757 " 15° " 59° "	71
Undecane	$C_{11}H_{24}$	180—184° " 356—363° "	0·765 " 16° " 61° "	78
Duodecane	$C_{12}H_{26}$	196—200° " 384—392° "	0·776 " 20° " 68° "	85
Tridecane	$C_{13}H_{28}$	216—218° " 421—424° "	0·792 " 20° " 68° "	92
Quatuordecane	$C_{14}H_{30}$	236—240° " 456—464° "	—	99
Quindecane	$C_{15}H_{32}$	255—260° " 491—500° "	—	106

American petroleum likewise yields a quantity of liquid boiling above 300° C. (572° F.), and doubtless containing paraffins of still higher order. Some specimens of the crude oil, as it issues from the ground, contain ethane, C_2H_6, and propane, C_3H_8, which are given off from it as gas at ordinary temperatures. In boring for the oil also, large quantities of gas escape, exhibiting the characters of methane; hence it is probable that in the great geological changes which have given rise to the separation of the petroleum, the whole series of paraffins have been formed from marsh gas upwards.

Solid paraffin is a colorless crystalline fatty substance, probably consisting of a mixture of several of the higher members of the series C_nH_{2n+2}. It is found native in the coal-measures, and other bituminous strata, constituting the minerals known as *fossil wax*, *ozocerite*, *hatchettin*, &c. It exists also in the state of solution in many kinds of petroleum, and may be separated by distilling off the more volatile portions, and exposing the remainder to a low temperature. In a similar manner also may solid paraffin be obtained from the tar of wood, coal, and bituminous shale. It was first prepared by Reichenbach from wood-tar. It is tasteless and inodorous, insoluble in water, slightly soluble in alcohol, freely in ether, and miscible in all proportions, when melted, with fixed or volatile oils. It burns with a very bright flame, and those varieties of it which melt at temperatures above 45° C. (113° F.) are very hard, and well adapted for making candles. Paraffin is largely used also as a substitute for sulphur for dipping matches; and Dr. Stenhouse has patented its application to woollen cloths, to increase their strength and make them waterproof. More extensive, however, are the uses of the liquid compounds of the paraffin series, known in commerce as *paraffin oil*, *photogene*, *solar oil*, *eupione*, &c. These oils are largely used for burning in lamps; and, when mixed with fatty oils, such as rape and cotton-seed oils, form excellent materials for lubricating machinery. For the former purpose they are exceedingly well adapted, as, with a proper supply of air, they give a much brighter light than that obtained from fatty oils containing oxygen, and are much cleaner in use.

It is necessary to observe, however, that natural petroleum and the oils obtained by the dry distillation of coal, &c., at low temperatures, are mixtures of a great number of paraffins differing greatly in volatility, and that to render them safe for burning in lamps of ordinary construction, they must be freed by distillation from the more volatile members of the series; otherwise they will take fire too easily, and, when they become heated, will

give off highly inflammable vapors, which, mixing with the air in the body of the lamp, may easily produce dangerously explosive mixtures; serious accidents have indeed arisen from this cause. It has been found by experience that it is not safe to use a paraffin oil which will take fire on the application of a match and burn continuously, at a temperature below 38° C. (100° F.).

Substitution-products of the Paraffins. — Paraffins subjected to the action of *bromine* or *chlorine*, give up a part, or in some cases the whole of their hydrogen in exchange for the halogen element. Thus equal volumes of chlorine and methane, CH_4, exposed to diffused daylight, yield the compound CH_3Cl, called chloromethane or methyl chloride: and, by further subjecting this product to the action of an excess of chlorine in direct sunshine, it may be successively converted into the more highly chlorinated compounds CH_2Cl_2, $CHCl_3$, and CCl_4. Ethane, C_2H_6, also yields, by a series of processes to be hereafter described, the substitution-products C_2H_5Cl, $C_2H_4Cl_2$, $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6; and similarly for the other compounds of the series. These bodies, which may be regarded as compounds of chlorine and other halogen elements with the radicals $(CH_3)'$, $(CH_2)''$, $(CH)'''$, &c., are called *haloïd ethers;* the more important of them will be specially described in connection with the corresponding alcohols. When treated with water or aqueous alkalies, they exchange the haloïd element for an equivalent quantity of hydroxyl, (HO), thereby producing alcohols (p. 468); and, on the other hand, they may be formed from the alcohols by the action of the chlorides, bromides, and iodides of hydrogen or phosphorus.

Nitric acid attacks the higher members of the paraffin series, forming *nitro-compounds;* octane, C_8H_{18}, thus treated, yields the compound, $C_8H_{17}(NO_2)$. The lower paraffins, on the other hand, are not affected in the slightest degree by nitric acid; but by indirect means compounds may be formed, having the composition of paraffins, in which the hydrogen is more or less replaced by nitryl; for example, *trinitromethane* or *nitroform*, $CH(NO_2)_3$.

Isomerism in the Paraffin series. — It has already been mentioned that these hydrocarbons are sometimes regarded as hydrates of the univalent alcohol radicals C_nH_{2n+1}, — methane, for example, as methylhydride, $H.CH_3$, ethane as ethyl hydride, $H.C_2H_5$. This view of their constitution is suggested by their formation by the action of water on the zinc compounds of the same radicals; *e. g.*:

$Zn(CH_3)_2$	+	$2OH_2$	=	ZnH_2O_2	+	$2(H.CH_3)$;
Zinc methyl.		Water.		Zinc hydrate.		Methyl hydride.

and by the facility with which they give up one atom of hydrogen in exchange for chlorine and bromine, whereas the replacement of the remaining hydrogen-atoms is much more difficult. On the other hand, all these hydrocarbons, except methane, may be regarded as compounds of two equivalents or half-molecules of alcohol radicals C_nH_{2n+1}, thus:

C_2H_6	=	$H.C_2H_5$	or	$CH_3.CH_3$,
Ethane.		Ethyl hydride.		Dimethyl.

C_3H_8	=	$H.C_3H_7$	or	$CH_3.C_2H_5$,
Propane.		Propyl hydride.		Methyl-ethyl.

C_4H_{10}	=	$H.C_4H_9$	or	$C_2H_5.C_2H_5$	or	$CH_3.C_3H_7$,
Quartane.		Quartyl hydride		Diethyl.		Methyl-propyl.

This latter view appears to accord with their formation by the action of

zinc on the iodides of the alcohol radicals, which is similar to that of hydrogen by the action of zinc on hydriodic acid; thus:

$$\underset{}{Zn} + \underset{\text{Hydrogen iodide.}}{2HI} = \underset{\text{Zinc iodide.}}{ZnI_2} + \underset{\text{Hydrogen.}}{H_2},$$

$$Zn + \underset{\text{Ethyl iodide.}}{2C_2H_5I} = ZnI_2 + \underset{\text{Diethyl.}}{C_2H_5 . C_2H_5}$$

$$Zn + \underset{\text{Methyl iodide.}}{CH_3I} + \underset{\text{Ethyl iodide.}}{C_2H_5I} = ZnI_2 + \underset{\text{Methyl-ethyl.}}{CH_3 . C_2H_5},$$

The first three hydrocarbons of the series, however, viz., CH_4, C_2H_6, C_3H_8, exhibit exactly the same physical and chemical properties in whatever way they may be prepared; and indeed the constitutional formulæ of these bodies, viz.

$$CH_4 \qquad \begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} \qquad \begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_3 \end{matrix}$$

show that they are not susceptible of isomeric modification, inasmuch as there is but one way in which the carbon-atoms in either of them can be grouped: in ethane each carbon-atom is directly combined with three hydrogen-atoms and the other carbon-atom; and whether we regard it as

$$H—\begin{matrix} CH_3 \\ | \\ CH_2 \end{matrix},$$

ethyl hydride, or as dimethyl, $H_3C—CH_3$, this arrangement remains the same. In propane, C_3H_8, each carbon-atom is directly combined with at most two other carbon-atoms, and there is no other way in which the atoms can be arranged.

But if we look at the formula of the 4-carbon paraffin, C_4H_{10}, we see that it may be written in either of the following forms:

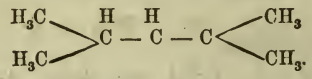
$$\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2 \\ | \\ CH_3 \end{matrix} \qquad \begin{matrix} H_3C & CH_3 \\ & \diagdown\diagup \\ & CH \\ & | \\ & CH_3 \end{matrix}$$

in the first of which, neither of the carbon-atoms is directly united with more than two others, whereas in the third, one of the carbon-atoms is directly combined with three others. The first may be represented, either as *propyl-methane*, $C\left\{\begin{matrix} CH_2CH_2CH_3 \\ H_3 \end{matrix}\right. = C\left\{\begin{matrix} CH_2C_2H_5 \\ H_3 \end{matrix}\right. = C\left\{\begin{matrix} C_3H_7 \\ H_3 \end{matrix}\right.$, or as *diethyl*, $H_5C_2 . C_2H_5$, according to the manner in which we may suppose it to be divided; the second as *trimethyl methane*, $C\left\{\begin{matrix} (CH_3)_3 \\ H \end{matrix}\right.$, or *isopropyl methane*, $C\left\{\begin{matrix} CH(CH_3)_2 \\ H_3 \end{matrix}\right.$, the radical $CH(CH_3)_2$ being called *isopropyl*, to distinguish it from normal propyl, $CH_2(C_2H_5)$.

From recent observations* it appears that all hydrocarbons of known structure may be divided into four groups, viz.: 1. Those in which each carbon-atom is directly associated with at most two other carbon-atoms. 2. Those in which one carbon-atom is associated with three carbon-atoms,

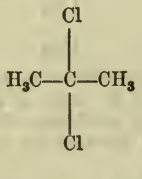
* Schorlemmer, Proceedings of the Royal Society, xvi. 34, 367.

or which contain the group isopropyl once. 3. Those which contain this group twice, such as di-isopropyl, or tetramethyl-ethane, $C_6H_{14} = C_2\left\{\begin{matrix}H(CH_3)_2,\\H(CH_3)_2\end{matrix}\right.$ produced by the action of zinc on isopropyl iodide; this compound may be represented by the constitutional formula:

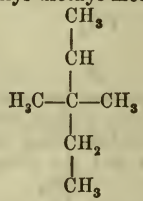


4. Those in which one carbon-atom is associated with four others, as in dimethyl-diethyl-methane, or carbdimethyl-diethyl, $C\left\{\begin{matrix}(CH_3)_2\\(C_2H_5)_2\end{matrix}\right.$, a compound produced by the action of zinc-ethyl, $Zn(C_2H_5)_2$, on dimethyl-dichloromethane, $C\left\{\begin{matrix}(CH_3)_2\\Cl_2\end{matrix}\right.$, the transformation being effected by the substitution of 2 atoms of ethyl for 2 atoms of chlorine:

Dimethyl-dichloro-methane.



Dimethyl-diethyl-methane.



The paraffins of each of these groups exhibit a regular increase in boiling point as they ascend in the series by successive addition of CH_2, and the boiling point of a paraffin containing a given number of carbon-atoms, is found to be lower in proportion as its structure is more complex. In the first and second groups the difference of boiling point, for each increment of CH_2, is about 31° C. (56° F.), whereas in the third it is only 25° C. (45° F.).

Second Series, C_nH_{2n}. — Olefines.

The hydrocarbons of this series are polymeric, as well as homologous with one another, inasmuch as their formulæ are all exact multiples of that of the lowest CH_2. The lower members of the series are gaseous at ordinary temperatures, the higher members are solid, and the intermediate compounds liquid. The names and formulæ of the known members of the olefine series are given in the following table, together with their melting and boiling points:

Name.			Formula.	Melting point.	Boiling point.
Ethene	or	Ethylene	C_2H_4	—	—
Propene	"	Propylene	C_3H_6	—	—17·8° C. 14° F.
Quartene	"	Butylene	C_4H_8	—	+3° " 37·4 "
Quintene	"	Amylene	C_5H_{10}	—	35° " 95 "
Sextene	"	Hexylene	C_6H_{12}	—	68–70° " 154–158 "
Septene	"	Heptylene	C_7H_{14}	—	95° " 203° "
Octene	"	Octylene	C_8H_{16}	—	115–117° " 239–242° "
Nonene	"	Nonylene	C_9H_{18}	—	140° " 284° "
Decene	"	Paramylene	$C_{10}H_{20}$	—	160° " 320° "
Sexdecene	"	Cetene	$C_{11}H_{32}$	—	275° " 527° "
Septivigintine	"	Cerotene	$C_{27}H_{54}$	57° C. 135° F.	(?) (?)
Trigintene	"	Melene	$C_{30}H_{60}$	62° " 144° "	375° (?) " 707° (?) "

Methene, CH_2, the lowest term of the series, does not appear to be capable of existing in the separate state; but its oxygen analogue, carbon monoxide or carbonyl, CO, is a well-known compound, which has been already described (p. 168).

Formation of the Olefines. — 1. By abstraction of the elements of water from the alcohols of the series $C_nH_{2n+2}O$, homologous with common alcohol, under the influence of powerful dehydrating agents, such as oil of vitriol, phosphoric oxide, or zinc chloride; thus:

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} - \underset{\text{Water.}}{OH_2} = \underset{\text{Ethene.}}{C_2H_4}$$

The preparation of ethene, or olefiant gas, by heating common alcohol with oil of vitriol, has been already described (p. 169). Quintyl, or amyl alcohol, $C_5H_{12}O$, distilled with zinc chloride, yields — besides the corresponding olefine, quintene or amylene, C_5H_{10} — a number of others polymeric with it; besides quintane, C_5H_{12}, and its homologues, and hydrocarbons containing a smaller proportion of hydrogens than the olefines.

2. By passing the vapors of the haloïd compounds of the monad radicals, C_nH_{2n+1}, over lime at a dull red heat; *e. g.:*

$$\underset{\substack{\text{Quintyl}\\\text{chloride.}}}{2C_5H_{11}Cl} + \underset{\text{Lime.}}{CaO} = \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2} + \underset{\text{Water.}}{OH_2} + \underset{\text{Quintene.}}{2C_5H_{10}}$$

3. By the decomposition of the paraffins at the moment of their formation by the action of zinc or sodium on the alcoholic iodides of the monad alcohol-radicals C_nH_{2n+1} (see p. 475).

4. By the action of these same iodides on the sodium compounds of the same radicals; for example:

$$\underset{\substack{\text{Ethyl}\\\text{iodide.}}}{C_2H_5I} + \underset{\substack{\text{Sodium}\\\text{ethyl.}}}{C_2H_5Na} = \underset{\substack{\text{Sodium}\\\text{iodide.}}}{NaI} + \underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Ethane.}}{C_2H_6}$$

5. By decomposition of the hydrates of ammonium bases containing four atoms of a monad alcohol-radical (p. 471), these compounds when heated splitting up into a tertiary monamine (p. 470) and an olefine; thus:

$$\underset{\substack{\text{Tetrethylammo-}\\\text{nium hydrate.}}}{N(C_2H_5)_4(HO)} = \underset{\substack{\text{Triethyl-}\\\text{ammine.}}}{N(C_2H_5)_3} + \underset{\text{Water.}}{OH_2} + \underset{\text{Ethene.}}{C_2H_4}$$

6. Olefines are formed by the decomposition of acetates and butyrates at a red heat, distilling over together with several other products, from which they are separated by combining them with bromine, and heating the resulting bromine-compounds, $C_nH_{2n}Br_2$, to 275° C. (527° F.), with copper, water, and potassium iodide. In this manner Berthelot has obtained ethene, propene, quartene, and quintene.

7. Several of the olefines may be produced by direct synthesis from other hydrocarbons of simpler constitution.

a. Ethene is formed by the action of nascent hydrogen upon ethine or acetylene (p. 484):

$$\underset{\text{Ethine.}}{C_2H_2} + H_2 = \underset{\text{Ethene.}}{C_2H_4}$$

β. Propene, C_3H_6, is formed by passing a mixture of methane and carbon monoxide (oxymethene) through a red-hot tube:

$$2CH_4 + CO = OH_2 + C_3H_6.$$

Also by the action of methenyl chloride (chloroform) on zinc ethide:

$$2CHCl_3 + 3Zn(C_2H_5)_2 = 3ZnCl_2 + 4C_3H_6 + 2CH_4.$$

γ. Quintene, or amylene, C_5H_{10}, or a compound isomeric with it, is formed by the action of zinc ethide on propenyl (allyl) iodide:

$$2C_3H_5I + Zn(C_2H_5)_2 = ZnI_2 + 2C_5H_{10}.$$

δ. Sextene, or hexylene, C_6H_{12}, is obtained in combination with hydriodic acid by the action of that acid on mannite, which is a sugar having the composition of a hexatomic alcohol:

$$\underset{\text{Mannite.}}{C_6H_8(HO)_6} + 11HI = 6OH_2 + 5I_2 + \underset{\substack{\text{Sextene}\\\text{hydriodide.}}}{C_6H_{12}.HI};$$

and this hydriodide, heated with potassium hydrate, yields the hydrocarbon:

$$C_6H_{12}.HI + OKH = KI + OH_2 + C_6H_{12}.$$

ε. Quartene, or butylene, C_4H_8, is obtained by precisely similar reactions from erythrite, which is also a saccharine substance having the composition of a tetratomic alcohol, $C_4H_6(HC)_4$.

Reactions.—1. The olefines are dyad radicals, uniting with 2 atoms of chlorine, bromine, &c., and with one atom of oxygen.

2. The chlorides, bromides, and other haloïd compounds of the olefines, treated with an alcoholic solution of potash, give up one atom of hydrogen and one atom of the haloïd element, yielding an olefine in which one atom of hydrogen is replaced by chlorine, bromine, &c., together with water and a haloïd salt of potassium; thus:

$$\underset{\text{Ethene bromide.}}{C_2H_4Br_2} + OKH = KBr + OH_2 + \underset{\text{Bromethene.}}{C_2H_3Br}.$$

The resulting chlorinated, brominated, or iodated compound can, in its turn, take up 2 atoms of chlorine, bromine, or iodine, forming a body which can likewise give up hydrochloric, hydrobromic, or hydriodic acid, under the influence of alcoholic potash; the body thus formed can again take up 2 atoms of chlorine, bromine, or iodine; then give up HCl, HBr, or HI; and thus, by a series of perfectly similar reactions, we at length arrive at bodies consisting of the primitive olefine with all its hydrogen replaced by chlorine, bromine, or iodine, and the dichlorides, dibromides, and di-iodides of these last-mentioned bodies: thus, from ethene may be derived the two following series of brominated compounds:—

Ethene . . . . C_2H_4	Ethene bromide . . . . $C_2H_4Br_2$
Bromethene . . C_2H_3Br	Bromethene bromide . . $C_2H_3Br . Br_2$
Dibromethene . $C_2H_2Br_2$	Dibromethene bromide . . $C_2H_2Br_2 . Br_2$
Tribromethene . C_2HBr_3	Tribromethene bromide . $C_2HBr_3 . Br_2$
Tetrabromethene C_2Br_4	Tetrabromethene bromide . $C_2Br_4 . Br_2$

These compounds will be more particularly described in connection with the corresponding alcohols.

3. A monochlorinated or monobrominated olefine may give up the atom of chlorine or bromine which it contains, in the form of hydrochloric or hydrobromic acid, whereby it is reduced to a hydrocarbon of the following series, C_nH_{2n-2}. This reaction may take place at 130°—150° C. (266°—302 F.), under the influence of alcoholic potash, or, better, of sodium ethylate (obtained by dissolving sodium in anhydrous alcohol); thus:

$$\underset{\text{Bromethene.}}{C_2H_3Br} + \underset{\substack{\text{Sodium}\\\text{ethylate.}}}{C_2H_5NaO} = \underset{\substack{\text{Sodium}\\\text{bromide.}}}{NaBr} + \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5(HO)} + \underset{\text{Ethine.}}{C_2H_2}.$$

4. Ethene bromide and its homologues, treated with silver acetate or potassium acetate, exchange their bromine for an equivalent quantity of the halogenic residue of the acetate, $C_2H_3O_2$ (p. 472), giving rise to diatomic acetic ethers; thus:

$$\underset{\text{Ethene bromide.}}{(C_2H_4)''Br_2} + \underset{\text{Potassium acetate.}}{2C_2H_3O_2K} = \underset{\text{Potassium bromide.}}{2KBr} + \underset{\text{Ethene diacetate.}}{(C_2H_4)''(C_2H_3O_2)_2};$$

and these ethers, distilled with a caustic alkali, yield diatomic alcohols or glycols; for example:

$$\underset{\text{Ethene diacetate.}}{(C_2H_4)''C_2H_3O_2)_2} + 2OHK = \underset{\text{Potassium acetate.}}{2C_2H_3O_2K} + \underset{\text{Ethene alcohol.}}{(C_2H_4)''(OH)_2}.$$

5. The bromides, $C_nH_{2n}Br_2$, heated to 275° C. (527° F.) with a mixture of potassium iodide, copper, and water, give up their bromine and reproduce the original olefine, together with other hydrocarbons (p. 476).

6. Some olefines, when briskly shaken up with strong snlphuric acid, unite with it, forming acid ethers of sulphuric acid, which contain the monatomic alcoholic radicals corresponding to the olefines; thus:

$$\underset{\text{Ethene.}}{C_2H_4} + \underset{\text{Sulphuric acid.}}{SO_4H_2} = \underset{\text{Ethyl-sulphuric acid.}}{SO_4 . C_2H_5 . H};$$

and these acid ethers distilled with water reproduce sulphuric acid, and the monatomic alcohol corresponding to the olefine:

$$\underset{\text{Ethyl-sulphuric acid.}}{SO_4 . C_2H_5H} + \underset{\text{Water.}}{H(OH)} = SO_4H_2 + \underset{\text{Ethyl alcohol.}}{C_2H_5(OH)}.$$

With fuming sulphuric acid (which contains sulphuric oxide in solution) the olefines yield sulpho-acids which are isomeric with the preceding, but are not decomposed by water, with formation of an alcohol.

7. Olefines unite with hydrochloric, hydrobromic, and hydriodic acids; and the resulting compounds treated with silver oxide in presence of water, give rise to two different reactions which go on simultaneously, one part of the compound exchanging its halogen element for hydroxyl, and thereby producing an alcohol, while another portion gives up hydrochloric, hydrobromic, or hydriodic acid, reproducing the original olefine:

$$\underset{\text{Hexylene hydriodide.}}{2(C_6H_{12} . HI)} + OAg_2 + OH_2 = 2AgI + \underset{\text{Hexyl alcohol.}}{2C_6H_{14}O}$$

$$\underset{\text{Hexylene hydriodide.}}{2(C_6H_6 . HI)} + OAg_2 = 2AgI + OH_2 + \underset{\text{Hexylene.}}{2C_6H_6}.$$

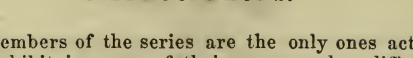
The greater number of the olefines are not of sufficient importance to require special description in this work. Ethene has been already described (p. 170). Quintene, or amylene, and a few others will be noticed in connection with the corresponding alcohols.

Isomerism in the Olefine series.—From theoretical considerations, it might be expected that each member of the olefine series would exist in two isomeric modifications, the one being a dyad radical, and the other a saturated hydrocarbon; the compound C_2H_4, for example, might exhibit the two modifications represented below:

$$\underset{\text{Dyadic.}}{\begin{matrix}-CH_2\\ |\\ -CH_2\end{matrix}} \qquad \underset{\text{Saturated.}}{\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix}}$$

But the dyadic members of the series are the only ones actually known. These, however, exhibit in some of their compounds a different kind of isomerism, which does not affect their equivalent value.

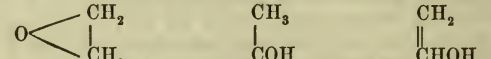
a. The dichlorides of the olefines are isomeric with the monochlorinated chlorides of the monad alcohol radicals, C_nH_{2n+1}; for example:



Ethene dichloride. Monochlorinated ethyl chloride.

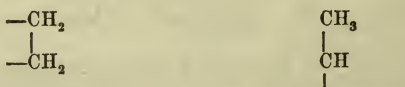
Both these compounds, when treated with alcoholic potash, yield the same product, namely, vinyl chloride, C_2H_3Cl; but they differ in boiling point, the first boiling at 85° C. (185° F.), the second at 64° C. (147° F.)

β. The oxides of the olefines are isomeric with the corresponding aldehydes, and with the alcohols of the series $C_nH_{2n-1}OH$



Ethene oxide. Acetic aldehyde. Vinyl alcohol.

The dyad radical, called *ethidene*, or *ethylidene*, which may be supposed to exist in aldehyde and in monochlorinated ethyl chloride, has not been isolated: it probably differs from ethene in the manner shown by the following formulæ:



Ethene. Ethidene.

Similar instances of isomerism are observed in the compounds of the other members of the olefine series.

Third Series, C_nH_{2n-2}.

Of these hydrocarbons five only have as yet been prepared, viz.:

Ethine	or Acetylene,	C_2H_2
Propine	" Allylene,	C_3H_4
Quartine	" Crotonylene,	C_4H_6
Quintine	" Valerylene,	C_5H_8
Sextine	" Diallyl,	C_6H_{10}.

The only general method of preparing these bodies consists in heating the monobrominated derivatives of the olefines, $C_nH_{2n-1}Br$, with sodium ethylate to 130°–150° C. (266°–302° F.):

$$C_nH_{2n-1}Br + C_2H_5NaO = NaBr + C_2H_5(HO) + C_nH_{2n-2}.$$

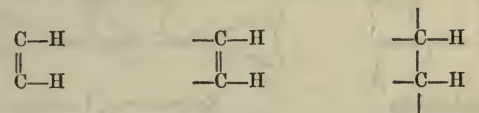
Sodium ethylate. Ethyl alcohol.

Ethine and propine, which are gaseous at ordinary temperatures, are separated from the alcohol vapor with which they are mixed, by passing the gas into an ammoniacal solution of cuprous chloride, whereby an explosive compound is precipitated, containing copper, carbon, hydrogen, and

oxygen; and this precipitate, treated with hydrochloric acid, yields the hydrocarbon in the pure state.

The other hydrocarbons of the series, which are liquid, do not form any precipitate with ammoniacal cuprous chloride; but they may be separated from excess of alcohol by addition of water, and further purified by distillation.

The hydrocarbons of this series should exhibit three isomeric modifications: saturated, dyadic, and tetradic, according to the manner in which the carbon atoms are united; thus, for the compound C_2H_2:



Saturated. Dyadic. Tetradic.

The actually known compounds are, however, all tetradic, being capable of uniting with four atoms of chlorine, bromine, and other monad elements, though they can also form half-saturated compounds containing only 2 atoms of a monad element.

When agitated with hydrobromic or hydriodic acid, they take up one or two molecules of these acids. The dihydrobromides and dihydriodides thus produced have the same composition as the dibrominated derivatives of the olefine series; thus:

$$C_n H_{2n-2} \cdot 2HBr = C_n H_{2n} Br_2.$$

The two classes of bodies are, however, isomeric, not identical.

Ethine, or Acetylene, C_2H_2.—This hydrocarbon is one of the constituents of coal gas. It is produced:—1. By synthesis from its elements. When an electric arc from a powerful voltaic battery passes between carbon poles in an atmosphere of hydrogen, the carbon and hydrogen unite in the proportion to form ethine.

2. By the action of heat upon ethene, or the vapor of alcohol, ether, or wood-spirit, or by passing induction-sparks through marsh-gas.

3. By passing the vapor of chloroform over ignited copper:

$$2CHCl_3 + Cu_6 = 3Cu_2Cl_2 + C_2H_2.$$

4. By the incomplete combustion of bodies containing carbon and hydrogen: for example:

$$\underset{\text{Methane.}}{4CH_4} + O_6 = 6OH_2 + \underset{\text{Ethine.}}{2C_2H_2}$$

$$\underset{\text{Ethene.}}{2C_2H_4} + O_2 = 2OH_2 + \underset{\text{Ethine.}}{2C_2H_2}$$

5. By passing a mixture of marsh-gas and carbon monoxide through a red-hot tube:

$$CH_4 + CO = OH_2 + C_2H_2.$$

6. By the action of alcohol potash on monobromethene:

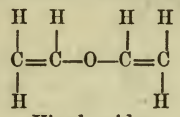
$$C_2H_3Br + OHK = KBr + OH_2 + C_2H_2.$$

The crude ethine obtained by either of these processes is purified in the manner above mentioned.

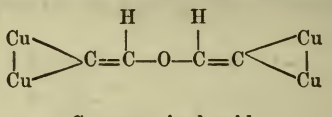
Ethine is a colorless gas of specific gravity 0·92, having a peculiar and unpleasant odor, moderately soluble in water, not condensed by cold or pressure. It burns with a very bright and smoky flame, one volume of the gas

consuming 2½ volumes of oxygen and producing 2 volumes of carbon dioxide. When mixed with *chlorine*, it detonates almost instantly, even in diffused daylight, with separation of carbon.

Ethine passed into an ammoniacal solution of *cuprous chloride* forms a red precipitate consisting of *cuproso-vinyl oxide*, $C_4Cu'_4H_2O$, or $(C_2Cu'_2H)_2O$, that is to say, vinyl-oxide $(C_2H_3)_2O$, having four of its hydrogen-atoms replaced by four atoms of apparently univalent copper.* The constitution of this compound may be understood from the following formulæ:



Vinyl oxide.



Cuproso-vinyl oxide.

Its formation from cuprous chloride and ethine is represented by the equation:

$$2Cu'_2Cl_2 + 2C_2H_2 + OH_2 = 4HCl + C_4Cu'_4H_2O.$$

On heating it with hydrochloric acid, the opposite reaction takes place, cuprous chloride and water being reproduced, and pure ethine evolved as gas.

When this copper compound is heated with zinc and dilute ammonia, the nascent hydrogen thereby evolved unites with the elements of ethine, producing ethene:

$$C_4Cu_4H_2O + 2H_2 = Cu_4 + OH_2 + 2C_2H_2,$$

and

$$C_2H_2 + H_2 = C_2H_4.$$

Ethine, briskly agitated with strong *sulphuric acid*, is absorbed, producing vinyl-sulphuric acid, $C_2H_4SO_4$:

$$C_2H_2 + SO_4H_2 = SO_4(C_2H_3)H;$$

and this acid, distilled with water, is resolved into sulphuric acid and vinyl alcohol:

$$\underset{\text{Vinyl-sulphuric acid.}}{SO_4(C_2H_3)H} + OH_2 = SO_4H_2 + \underset{\text{Vinyl alcohol.}}{C_2H_3(OH)}$$

Ethine unites with *bromine*, forming a dibromide, $C_2H_2Br_2$.

Bromethine, or *Bromacetylene*, C_2HBr, is produced by the action of alcoholic potash on dibromethene dibromide:

$$C_2H_2Br_2 . Br_2 = HBr + Br_2 + C_2HBr.$$

It is a spontaneously inflammable gas, which liquefies under a pressure of three atmospheres, is soluble in water, and very soluble in dibromethene. It unites with bromine, forming the compound, $C_2HBr . Br_2$, and when passed into an ammoniacal solution of cuprous chloride, yields a precipitate of cuproso-vinyl oxide.

Propine, or Allylene, C_3H_4.—This compound is produced by the action of sodium ethylate on bromopropene:

$$\underset{\text{Bromo-propene}}{C_3H_5Br} + \underset{\text{Sodium ethylate}}{C_2H_5NaO} = NaBr + \underset{\text{Ethyl alcohol}}{C_2H_5(HO)} + \underset{\text{Propine}}{C_3H_4}$$

* See page 354.

its formation being a particular case of the general reaction given on page 484. It is a colorless gas, having an unpleasant odor, burning with a smoky flame, and forming, with mercurous salts, a gray precipitate; with silver salts, a white precipitate; and with cuprous chloride a yellow precipitate analogous in composition to that formed by ethine. With *bromine* it forms the compounds $C_3H_4Br_2$, and $C_3H_4Br_4$.

Quartine, or **Crotonylene**, C_4H_6. — Produced by the action of sodium ethylate on bromoquartene. It is liquid below 15° C. (59° F.), but volatilizes very quickly if not cooled by ice. It has a very strong, somewhat alliaceous odor, boils at about 18° C. (64° F.), and distils between 18° and 24° C. (75° F.). *Bromine* dropped into this liquid, cooled by a freezing mixture, yields *dibromoquartine*, $C_4H_6Br_2$, a liquid heavier than water, and distilling, with partial decomposition, between 148° and 158° C. (298°–316° F.). This dibromide, left in contact for some days with excess of bromine, is converted into the *tetrabromide*, $C_4H_6Br_4$, a crystalline solid, isomeric with dibromo-quartene dibromide, $C_4H_6Br_2 . Br_2$.

Quintine, or **Valerylene**, C_5H_8, is obtained by heating quintene bromide with alcoholic potash (which abstracts hydrobromic acid), distilling the liquid separated from the product by water, and collecting that which passes over between 44° and 46° C. (111°–115° F.):

$$C_5H_{10}Br_2 \ - \ 2HBr \ = \ C_5H_8.$$

Quintine is a colorless, very mobile liquid, which floats on water, and is nearly insoluble therein. It has a pungent alliaceous odor, boils at 44° to 46°, and has a vapor-density of 2·356; it is not absorbed by ammoniacal cuprous chloride.

Quintine forms two series of compounds: the one composed of incomplete bodies still capable of fixing two atoms of chlorine, bromine, or other monad element, or one molecule of hydrobromic or hydrochloric acid; the other composed of saturated bodies:

Dyadic.		*Saturated.*	
Dibromide . .	$C_5H_8Br_2$	Tetrabromide .	C_5HBr_4.
Monohydrobromide	$C_5H_8 . HBr$	Dibromo-hydrobromide .	$C_5H_8 . HBr . Br_2$
Monohydrochloride	$C_5H_8 . HCl$	Dihydrobromide .	$C_5H_8 . H_2Br_2$
Monohydriodide .	$C_5H_8 . HI$	Dihydrochloride	$C_5H_8 . H_2Cl_2$
Monoacetate . .	$C_5H_8\left\{\begin{matrix}H\\C_2H_3O_2\end{matrix}\right.$	Diacetate . .	$C_5H_8\left\{\begin{matrix}H_2\\(C_2H_3O_2)_2\end{matrix}\right.$
Monohydrate . .	$C_5H_8\left\{\begin{matrix}H\\OH\end{matrix}\right.$	Dihydrate . .	$C_5H_8\left\{\begin{matrix}H_2\\(OH)_2\end{matrix}\right.$

The bromides, hydrobromides, hydrochlorides, and hydriodides are formed by direct combination; the acetates by heating the dihydrobromide in sealed tubes with silver acetate suspended in ether; the hydrates by treating the corresponding acetates with solid potash. These compounds are all liquid at ordinary temperatures. The dibromide, treated with potash in alcoholic solution, is converted, by abstraction of hydrobromic acid, into *quintone*, or *valylene*, C_5H_6 (= $C_5H_8Br_2$—2HBr).

Sextine, or **Diallyl**, C_6H_{10}, is produced: 1. By decomposing allyl iodide, C_3H_5I, with an alloy of tin and sodium. 2. Together with many other products by heating allyl iodide in sealed tubes with zinc ethide. It is a liquid which boils at 58° C. (136° F.), and forms two series of compounds, one saturated, the other dyadic, analogous to those of quintine, and obtained by similar processes.*

* A. Wurtz, Ann. Chim. Phys. [4], iii. 129. — Jahresbericht für Chemie, 1864, p. 210.

Fourth Series, C_nH_{2n-4}.

The known hydrocarbons of this series are *quintone*, or *valylene*, C_5H_6, produced by abstraction of hydrogen from quintine, C_5H_8; and certain volatile oils called *terpenes*, having the composition $C_{10}H_{16}$, and existing ready-formed in plants. The former is sexvalent and quadrivalent; the latter are quadrivalent and bivalent.

Quintone, or Valylene, C_5H_6, is formed, as already observed, by the action of alcoholic potash on quintine dibromide, $C_5H_8Br_2$, and passes over, together with a little quintine, between 45° and 50° C. (113°–122° F.). It may be obtained pure by treating the mixture with ammoniacal cuprous chloride, which precipitates the quintone, but not the quintine; and on warming the precipitate with dilute hydrochloric acid, the quintine passes over, and may be condensed by a freezing mixture. It is a light liquid, boiling at about 50° C. (122° F.) With *bromine*, in a freezing mixture, it forms a crystalline mass, consisting of *quintone hexbromide*, $C_5H_6Br_6$, saturated with a thick liquid, which is a mixture of the compounds $C_5H_6Br_6$, $C_5H_6Br_4$, and probably $C_5H_6Br_2$.

Terpenes, $C_{10}H_{16}$.—These bodies are volatile oils, existing in plants, chiefly of the coniferous and aurantiaceous orders; they have not yet been formed by any artificial process. The most important member of the group is *turpentine oil*, which is contained in the wood, bark, leaves, and other parts of pines, firs, and other coniferous trees, and is usually prepared by distilling crude turpentine, the oleo-resinous juice which exudes from incisions in the bark of the trees, either alone or with water. It was formerly supposed that all the volatile oils thus obtained, and having the composition $C_{10}H_{16}$, were identical in chemical and physical properties; but recent investigations, especially those of Berthelot, have shown that the turpentine oils obtained from different sources exhibit considerable diversities in their physical, and more especially in their optical properties; further, that most kinds of turpentine oil are mixtures of two or more isomeric or polymeric hydrocarbons, differing in physical and sometimes also in chemical properties. These modifications are often produced by the action of heat and of chemical reagents during the purification of the oil.

The several varieties of turpentine oil, when purified by repeated rectification with water, are colorless mobile liquids, having a peculiar aromatic but disagreeable odor. They are insoluble in water, slightly soluble in aqueous alcohol, miscible in all proportions with absolute alcohol, ether, and carbon disulphide. They dissolve iodine, sulphur, phosphorus, and many organic substances which are insoluble in water, such as fixed oils and resins, and are therefore used for making varnishes.

The principal varieties are, French turpentine oil, obtained from the French or Bordeaux turpentine of *Pinus maritima*, and English turpentine oil, from the turpentine collected in Carolina and other Southern States of the American Union, from *Pinus Australis* and *Pinus tæda*.

French turpentine oil, when purified by neutralizing it with an alkaline carbonate, and then distilling it, first over the water-bath, and then in a vacuum (by which treatment all transformation of the product by heat or by reagents is avoided), consists mainly of a hydrocarbon, $C_{10}H_{16}$, called *terebenthene*. It has a specific gravity of 0·864, boils at 161° C. (322° F.), and turns the plane of polarization of a ray of light to the left. English turpentine oil, treated in a similar manner, yields, as its chief constituent, a liquid called *australene*, or *austraterebenthene*, having the same specific gravity and boiling point as terebenthene, but turning the plane of polarization to the right.

When pure turpentine oil (terebenthene or australene) is heated to 200°–250°, it undergoes a molecular transformation, and may then be separated by distillation into two oils, one called *austrapyrolene*, isomeric with the original oil, and boiling at 176° to 178° C. (348°–352° F.); the other, called *metaterebenthene*, polymeric with the original oil, having the formula $C_{20}H_{32}$, and boiling at a temperature above 360° C. (680° F). Both are levorotatory, the latter exhibiting the greater amount of rotatory power.

Turpentine oil treated with *boron fluoride* or strong *sulphuric acid*, is transformed into two hydrocarbons having no action on polarized light. The one, called *terebene*, has the formula $C_{10}H_{16}$, and boils at 160° C. (320° F.); the other, called *colophene*, or *diterebene*, consists of $C_{20}H_{32}$, and boils at a very high temperature.

By the action of *sodium stearate* on a solid compound of turpentine oil and hydrochloric acid to be presently described, a crystallized hydrocarbon, $C_{10}H_{16}$, called *camphene*, is formed, which turns the plane of polarization to the left or to the right, according as it has been formed from French or from English turpentine oil. If *sodium acetate* be used in its preparation in place of the stearate, the same hydrocarbon is obtained, but it is then optically inactive.

Turpentine oil exposed to the *air* absorbs oxygen, which then, as in all slow combustions, acquires the properties of ozone, and subsequently enters into combination with the hydrocarbon, forming resinous products. *Nitric acid*, and other powerful oxidizing agents, convert turpentine oil into a number of acid products of complex constitution. Strong nitric acid acts very violently on turpentine oil, sometimes setting it on fire.

Chlorine is absorbed by turpentine oil, with evolution of heat, sometimes sufficient to produce inflammation. When paper soaked in rectified turpentine oil is introduced into a vessel filled with chlorine, the turpentine takes fire, and a quantity of black smoke is produced, together with white fumes of hydrochloric acid. *Bromine* acts in a similar manner. *Iodine* is dissolved by turpentine oil, forming at first a green solution, which afterwards becomes hot, and gives off hydriodic acid. When a considerable quantity of iodine is suddenly brought in contact with turpentine oil, explosion frequently ensues. Turpentine oil distilled with *chloride of lime* and *water*, yields chloroform.

Compounds of Turpentine oil.— Turpentine oil forms several compounds with *hydrochloric acid*. The gaseous acid converts it into the *monohydrochloride*, $C_{10}H_{16}.HCl$. On the other hand, when the oil is subjected for several weeks to the action of the strong aqueous acid, crystals of a *dihydrochloride*, $C_{10}H_{16}.2HCl$, are obtained. This latter compound is also formed by the action of hydrochloric acid gas on *lemon oil;* hence it is called *citrene dihydrochloride*. By the action of hydrochloric acid on terebene, the compound $C_{20}H_{32}.HCl$ is formed, called *diterebene hydrochloride*. Lastly, when a current of hydrochloric acid gas is passed through a solution of turpentine oil in acetic acid, the compound $C_{20}H_{32}.3HCl$ is produced, called *dipyrolene hydrochloride*.

Hydrobromic and *hydriodic acids* form, with oil of turpentine, compounds analogous in composition to the hydrochlorides; the dihydriodide, however, has not been obtained from turpentine oil itself.

Whatever method may be adopted for preparing the hydrochlorides, hydrobromides, or the monohydriodide of turpentine oil, there are always two isomeric modifications obtained — one liquid, the other solid and crystalline. The crystallized monohydrochloride is sometimes, though inappropriately, designated as *artificial camphor*, and the dihydrochloride as *lemon camphor*.

Hydrates of Turpentine oil.— The terebenthenes unite with *water* in several proportions, yielding the following compounds:

$C_{10}H_{16} \cdot 3OH_2$	$C_{10}H_{16} \cdot 2OH_2$	$C_{10}H_{16} \cdot OH_2$	$2C_{10}H_{16} \cdot OH_2$
Terpin hydrate.	Terpin.	Terpintin hydrate.	Terpinol.

Terpin hydrate, $C_{10}H_{16} \cdot 2OH_2 \cdot$ Aq. (also called *Turpentine-camphor* and *Hydrate of Turpentine-oil*), is frequently deposited in crystals from turpentine oil containing water; its production is favored by the presence of an acid. To prepare it, 8 vols. turpentine oil are mixed with 2 vols. nitric acid and 1 to 6 vols. alcohol; and the mixture is frequently shaken during the first few days, then left to itself in shallow vessels for several weeks. Brown crystals are thereby formed, which must be pressed, and then recrystallized from boiling water, with addition of animal charcoal.

Terpin hydrate usually crystallizes in large rhombic prisms; it dissolves sparingly in cold, easily in boiling water, easily also in alcohol and ether. At 100° C. (212° F.) it melts, gives off its water of crystallization, and is converted into terpin. The same change takes place on exposing the crystals to air dried over oil of vitriol.

Terpin, $C_{10}H_{16} \cdot 2OH_2$, melts at 103° C. (217° F.), and solidifies in the crystalline state on cooling. It sublimes at about 150°, in slender needles. It is dissolved with red color by strong sulphuric acid, and converted into turpentine oil. The same change takes place on boiling the terpin with dilute acids, heating it to 100° C. (212° F.) with zinc chloride, or to 160°–180° C. (320°–356° F.) with chloride of calcium, strontium, or ammonium. Terpin, or terpin hydrate, subjected to the action of gaseous or aqueous hydrochloric acid, or of the chlorides, bromides, or iodides of phosphorus, is converted into the crystallized dihydrochloride, dihydrobromide, or dihydriodide; this is in fact the only way of obtaining the last-mentioned compound. Terpin, distilled with phosphoric oxide, yields terebene and colophene (p. 485). Heated with acetic or butyric acid, or with benzoic chloride, it yields terebene and polyterebenes. When heated with acetic oxide, $(C_2H_3O)_2O$, to 140° C. (284° F), for not too long a time, it yields a compound containing $C_{10}H_{16} \cdot C_2H_4O_2 \cdot OH_2$.

Terpentin hydrate, $C_{10}H_{16} \cdot OH_2$, is sometimes obtained in the preparation of terpin, either together with the latter or alone. It is a liquid insoluble in water, and boiling at 200°–220° C. (392°–428° F.).

Terpinol, $2C_{10}H_{16} \cdot OH_2$, is produced when terpin is boiled with dilute hydrochloric or sulphuric acid, or when the dihydrochloride of terebene is boiled with water, alcohol, or alcoholic potash. It is a colorless, strongly refracting oil, optically inactive, and boiling with partial decomposition at 168° C. (334° F.).

The hydrocarbon, $C_{10}H_{16}$ (decone or terebenthene), acts as a quadrivalent radical, capable of uniting with four monad atoms, and therefore with two molecules of the acids HCl, HBr, and HI, thereby producing the dihydrochlorides above mentioned; but, like other tetrad radicals, it can also take up only two monad atoms, producing the monohydrochloride, &c. The same tetrad radical, by doubling itself, loses two units of equivalence,—just as two atoms of carbon when united are satisfied by six, and not by eight atoms of hydrogen, and forms the hydrocarbon, $C_{20}H_{32}$, which is sexvalent, and can therefore form such compounds as $C_{20}H_{32} \cdot 3HCl$. Further, this same hexad radical might form non-saturated compounds containing only four or two monad atoms; in reality, however, only those containing two monad atoms are known, such as $C_{20}H_{32} \cdot HCl$.

If in the several hydrochlorides each atom of chlorine be replaced by hydroxyl, HO, we obtain the formulæ of the several hydrates of turpentine oil; the hydrate corresponding to the hydrochlorate, $C_{20}H_{32} \cdot HCl$, has not, however, been prepared.

Volatile Oils isomeric with Turpentine Oil.—The following volatile or essential oils obtained from plants exhibit, like oil of turpentine, the composition $C_{10}H_{16}$.

Terpenes from Aurantiaceous plants.—These terpenes are distinguished by their fragrant odor. Lemon oil, obtained from the rind of the fruit of *Citrus limonum*, by pressure, or by distillation with water, consists mainly of citrene, $C_{10}H_{16}$, a hydrocarbon closely resembling terebenthene, having a specific gravity of 0·85 at 15°, boiling at 167° or 168°, turning the plane of polarization to the right. With water it forms a crystallized hydrate resembling terpin; with hydrochloric acid, a dihydrochloride, $C_{10}H_{16}.2HCl$, existing in a solid and a liquid modification, and a monohydrochloride, $C_{10}H_{16}.HCl$, apparently susceptible of similar modifications.

Similar oils are obtained from the rind of the sweet orange (*Citrus aurantium*), the bergamot (*C. bergamia*), the bigarade or bitter orange (*C. bigaradia*), the lime (*C. limetta*), the sweet lemon (*C. lumia*), and the citron (*C. medica*). Oil of neroli, obtained by distilling orange-flowers with water, is probably also a terpene when pure.

Terpenes from other sources.—The volatile oils of athamanta, beech, borneo (from *Dryabalanops camphora*), caoutchouc, caraway, camomile, coriander, elemi, gomart, hop, juniper, imperatoria, laurel, parsley, pepper, savin, thyme, valerian, and others, also the neutral oils of wintergreen (*Gaultheria procumbens*), and cloves, are isomeric with oil of turpentine. The oils of copaiba and cubebs are probably polymeric with it, their molecules containing $C_{20}H_{32}$.

Caoutchouc, or *India-rubber*, the thickened milky juice of several species of *Ficus*, *Euphorbia*, and other trees growing in tropical countries, is essentially a mixture of several hydrocarbons isomeric or polymeric with turpentine oil. When pure it is nearly white, the dark color of commercial caoutchouc being due to the effects of smoke and other impurities. It is softened but not dissolved by boiling water; it is also insoluble in alcohol. In pure ether, rectified petroleum, and coal-tar oil, it dissolves, and is left unchanged on the evaporation of the solvent. Oil of turpentine also dissolves it, forming a viscid, adhesive mass, which dries very imperfectly. At a temperature a little above the boiling point of water, caoutchouc melts, but never afterwards returns to its former elastic state. Few chemical agents affect this substance; hence its great use in chemical investigations, for connecting apparatus, &c. By destructive distillation it yields a large quantity of a thin, volatile, oily liquid, of naphtha-like odor, called *caoutchoucin*, which dissolves caoutchouc with facility. This oil, according to Mr. Greville Williams, is composed of two polymeric hydrocarbons: caoutchin, $C_{10}H_{16}$, boiling at 171° C. (340° F.), and isoprene, C_5H_8, boiling at 37° C. (99° F.).

Caoutchouc combines with variable proportions of sulphur. The mixtures thus obtained are called *vulcanized India-rubber;* they are more permanently elastic than pure caoutchouc.

Vulcanite, or *Ebonite*, is caoutchouc mixed with half its weight of sulphur, and hardened by pressure and heating. It is very hard, takes a high polish, and is used for making combs, knife-handles, buttons, &c. It is also especially distinguished by the large quantity of electricity which it evolves when rubbed; hence it makes an excellent material for the plates of electrical machines.

Gutta-percha, the hardened milky juice of *Isonandra gutta*, a large tree growing in Malacca and many of the islands of the Eastern Archipelago, is similar in composition to caoutchouc, and resembles it in many of its properties, but is harder and less elastic. It is quite insoluble in, and impervious to, water, and being also an excellent electric insulator, is extensively used as a casing for submarine telegraph wires. By dry distillation

it yields isoprene, caoutchin, and a heavy oil called *heveene*, probably polymeric with these bodies.

Volatile or Essential Oils in general.—The volatile oils obtained from plants mostly consist either of hydrocarbons isomeric or polymeric with turpentine oil, or of mixtures of those hydrocarbons with compounds of carbon, hydrogen, and oxygen. Thus valerian oil contains valeric acid, $C_5H_{10}O_2$; pelargonium oil contains pelargonic acid, $C_9H_{18}O_2$; rue oil contains capric aldehyde, $C_6H_{12}O$; wintergreen oil contains acid methyl salicate, $C_8H_8O_3$, the oxygenated compound being associated in each case with a terpene. Some consist essentially of aldehydes: thus bitter almond oil consists of benzoic aldehyde, C_7H_6O; the oils of cinnamon and cassia contain cinnamic aldehyde, C_7H_8O; and those of anise, star-anise, fennel, and tarragon, contain anethol, $C_{10}H_{12}O$. Those volatile oils which exist ready formed in living plants do not appear to contain any elements besides carbon, hydrogen, and oxygen. Sulphur is found only in certain oils resulting from a kind of fermentation process, as in the volatile oils of mustard and garlic; nitrogen, when it occurs, must be regarded as an impurity resulting from admixed vegetable tissue. Volatile oils are mostly procured by distilling the plant, or part of the plant, with water; their points of ebullition almost always lie above that of water; nevertheless, at 100° the oils emit vapor of very considerable tension, which is carried over mechanically, and condensed with the steam. The milky or turbid liquor obtained separates, when left at rest, into oil and water. Sometimes the oil is heavier than the water, and sinks to the bottom: sometimes the reverse happens. From parts of plants which are very rich in volatile oil, such as lemon and orange-peel, the oil may be extracted by pressure.

A few volatile oils are found in the bodies of animals,—oil of ants, for example.

Most volatile oils are colorless when pure; they often, however, have a yellow color arising from impurity; and a few, the oils of wormwood and camomile, for example, have a green or blue color, due to the presence of an oily compound of a very deep blue color, called *cerulein*. They have usually a powerful odor, and a pungent, burning taste. When exposed to the air, they frequently become altered by slow absorption of oxygen, and assume the character of resins. They mix in all proportions with fat oils, such as linseed, nut, colza, and whale oils, and dissolve freely both in ether and alcohol: from the latter solvent they are precipitated by the addition of water. Volatile oils communicate a greasy stain to paper, which disappears by warming; by this character any adulteration with fixed oils can be at once detected. Many volatile oils, when exposed to cold, separate into a solid crystalline compound called a *camphor* or *stearoptene*, and a liquid oil, which, for distinction, is sometimes called an *elæoptene*.

Fifth Series, C_nH_{2n-6}.—Aromatic Hydrocarbons.

The hydrocarbons of this series present peculiar interest on account of the many important derivatives, including alcohols, acids, bases, &c., to which they gave rise. The whole group of compounds thus formed are usually designated as aromatic bodies, on account of the peculiar and fragrant odors exhibited by some of them,—benzoic acid, for example.

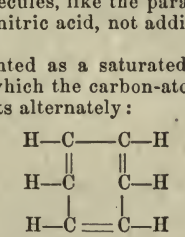
The known hydrocarbons of the aromatic series are:

Benzene	C_6H_6
Toluene	C_7H_8
Xylene	C_8H_{10}
Cumene	C_9H_{12}
Cymene	$C_{10}H_{14}$
Amylxylene	$C_{13}H_{20}$

They are all found (except the last) in the lighter part of the oil obtained by the destructive distillation of coal, and may be separated from one another by fractional distillation.

These hydrocarbons might be regarded as derived from the corresponding paraffins by abstraction of 8 atoms of hydrogen (*e. g.*, $C_6H_6=C_6H_{14}-H_8$), or from the olefines by abstraction of 6 atoms of hydrogen, &c.; and accordingly they might be expected to act as octovalent, sexvalent, quadrivalent, or bivalent radicals; and, in fact, cymene can combine with two atoms of chlorine, and benzene forms definite compounds with 6 atoms of chlorine and of bromine. But in nearly all cases the aromatic hydrocarbons react as saturated molecules, like the paraffins, yielding, when treated with chlorine, bromine, or nitric acid, not additive compounds, but substitution-products.

Benzene may be represented as a saturated molecule by the following constitutional formula, in which the carbon-atoms are united together by one and two combining units alternately:



The other hydrocarbons of the series may be derived from it by successive addition of CH_2, or by substitution of methyl, CH_3, for hydrogen; thus:

C_7H_8	=	$C_6H_5(CH_3)$	Methyl-benzene,
C_8H_{10}	=	$C_6H_4(CH_3)_2$	Dimethyl-benzene,
C_9H_{12}	=	$C_6H_3(CH_3)_3$	Trimethyl-benzene,
$C_{10}H_{14}$	=	$C_6H_2(CH_3)_4$	Tetramethyl-benzene.

Further, a hydrocarbon isomeric with dimethyl-benzene may be formed by the substitution of ethyl, C_2H_5, for 1 atom of hydrogen in benzene, viz., ethyl-benzene, $C_6H_5(C_2H_5)$; in like manner, methyl-ethyl-benzene, $C_6H_4(CH_3)(C_2H_5)$, and propyl-benzene, $C_6H_5(C_3H_7)$, are isomeric with trimethyl-benzene; diethyl-benzene, $C_6H_4(C_2H_5)_2$, with tetramethyl-benzene, &c., &c. It is easy to see that, in this manner, a large number of isomeric bodies may exist in the higher terms of the series.

Benzene, C_6H_6.—This hydrocarbon can be produced synthetically from its elements. When ethine, C_2H_2, which, as we have seen (p. 485), may be formed by the direct combination of carbon and hydrogen, is heated to a temperature somewhat below redness, it is converted into several polymeric modifications, the principal of which is *triethine* or *benzene*, $3C_2H_2=C_6H_6$.

Benzene is also formed in the dry distillation of many organic substances, and is contained in considerable quantity in the more volatile portion of coal-tar oil, from which it is now almost always prepared. To obtain it, the oil is repeatedly washed with dilute sulphuric acid and with potash, to remove the alkaline and acid products likewise existing in it; and the remaining neutral oil is submitted to repeated fractional distillation, the por-

tion which goes over between 80° and 90° C. (176°–194° F.) being collected apart. On cooling this distillate to —12° C. (10° F.), the benzene crystallizes out, and may be purified from adhering liquid substances by pressure. It is now prepared in immense quantities for the manufacture of aniline; but the commercial product is always impure, containing also the higher members of the aromatic series.

Pure benzene may be obtained by distilling benzoic acid with lime:

$C_7H_6O_2$	+	CaO	=	CO_3Ca	+	C_6H_6
Benzoic acid.		Lime.		Calcium carbonate.		Benzene.

Benzene is identical with the so-called *bicarburet of hydrogen*, discovered many years ago by Faraday in the liquid condensed during the compression of oil-gas (p. 172).

Pure benzene is a thin, limpid, colorless, strongly refracting liquid, having a peculiar ethereal odor. It has a density of 0·885 at 15·5° C. (60° F.), boils at 82° C. (180° F.), and solidifies at 3° C. (37° F.) to a white crystalline mass. It is nearly insoluble in water, but mixes with alcohol and ether. It dissolves iodine, sulphur, and phosphorus, and a large number of organic substances, fats and resins, for example, which are insoluble, or very sparingly soluble in water and alcohol; hence its use in many chemical preparations, and for removing grease-spots from articles of dress.

Benzene, passed in the state of vapor through a porcelain tube heated to bright redness, is partly resolved into hydrogen gas, containing a small quantity of ethine, and the following liquid products: (1) *diphenyl*, $C_{12}H_{10} = 2C_6H_6—H_2$; (2) *chrysene*, $C_{18}H_{12} = 3C_6H_6—H_6$; (3) *benzerythrene*, a solid, resinous, orange-colored body of unknown composition, which distils over in yellow vapors at a dull red heat; (4) *bitumene*, a blackish liquid, which remains in the retort at a dull red heat, and solidifies on cooling.*

Substitution-products of Benzene.— *Chlorine* and *bromine* act readily on benzene, forming substitution-products, in which the hydrogen-atoms are successively replaced by the halogen element; thus with chlorine the compounds

C_6H_5Cl, $C_6H_4Cl_2$, $C_6H_3Cl_3$, $C_6H_2Cl_4$, C_6HCl_5, C_6Cl_6

are obtained. The formation of the more highly chlorinated products is facilitated by the presence of iodine or of antimony pentachloride.

Monochlorobenzene, C_6H_5Cl, which may also be prepared by the action of phosphorus pentachloride on phenol, $C_6H_5(OH)$,—and is hence regarded as a chloride of the univalent radical *phenyl*, C_6H_5,—is a colorless liquid, heavier than water, and boiling at about 136°. When treated with nascent hydrogen (evolved from water by sodium or sodium amalgam) it is reconverted into benzene. *Dichlorobenzene*, $C_6H_6Cl_2$, is a crystalline solid; *trichlorobenzene* is a liquid which does not solidify at 0°. The more highly chlorinated benzenes are crystalline solids.

Monobromobenzene, C_6H_5Br, is a liquid; the compounds $C_6H_4Br_2$, and $C_6H_3Br_3$, are solid; similarly with the *iodobenzenes*.

These haloïd derivatives of benzene are comparatively stable compounds, which do not give off their chlorine, bromine, or iodine in exchange for hydroxyl or other radicals so easily as the corresponding derivatives of the paraffins (p. 478); thus monochlorobenzene or phenyl chloride, C_6H_5Cl, is not converted into hydroxyl-benzene or phenyl alcohol, $C_6H_5(OH)$, by treatment with water or alkalies.

* *Berthelot*, Bulletin de la Société Chimique de Paris, [2] vi. pp. 272, 279.

Nitrobenzenes.—Benzene dissolves readily in strong nitric acid, and on adding water to the solution, *nitrobenzene*, $C_6H_5(NO_2)$, separates out:

$$C_6H_6 + NO_2(OH) = OH_2 + C_6H_5NO_2.$$

It is a yellowish liquid, smelling like bitter almonds, and hence used in perfumery; it is known commercially by the incorrect name of *artificial oil of almonds*. By reducing agents it is converted into amidobenzene or aniline, $C_6H_5(N_2H)$, which will be described among organic bases.

Dinitrobenzene, $C_6H_4N_2O_4$, or $C_6H_4(NO_2)_2$, produced by warming benzene with a mixture of nitric and sulphuric acids, is a white substance, crystallizing in needles; by reducing agents it is converted into diamido-benzene or phenylene-diamine, $C_6H_4(NH_2)_2$.

Additive-compounds of Benzene.—Benzene, although, as already observed, it mostly reacts as a saturated molecule—exhibiting indeed in its chemical relations a very close resemblance to the paraffins—can nevertheless, under certain circumstances, take up 6 atoms, or 3 molecules, of chlorine or bromine, forming the compounds $C_6H_6Cl_6$, and $C_6H_6Br_6$. These are crystalline bodies, obtained by exposing benzene to sunshine in contact with chlorine or bromine; the former also by mixing the vapor of boiling benzene with chlorine. Benzene hexchloride melts at 132° C. (270° F.), and boils at 288° C. (550° F.), being partly resolved at the same time with hydrochloric acid and trichlorobenzene, $C_6H_6Cl_6 = 3HCl + C_6H_3Cl_3$. The same decomposition is quickly produced by heating the compound with alcoholic solution of potash. Benzene hexbromide exhibits a similar reaction.

Benzene is also capable of uniting directly with three molecules of *hypochlorous acid*, forming the compound $C_6H_9Cl_3O_3$, or $C_6H_6 . 3ClOH$, which crystallizes in thin colorless plates melting at about 10°, and is converted by alkalies into a saccharine compound called *phenose*, $C_6H_{12}O_6$, isomeric with glucose or grape-sugar:

$$C_6H_9Cl_3O_3 + 3OHK = 3KCl + C_6H_{12}O_6.$$

Toluene, C_7H_8, or **Methyl benzene**, $C_6H_5(CH_3)$.—This hydrocarbon, which may also be regarded as a compound of methyl with the univalent radical, phenyl, *i. e.*, as phenyl-methyl, $C_6H_5 . CH_3$, is produced: Synthetically (1) by the action of sodium on a mixture of bromobenzene (phenyl bromide), and methyl iodide:

$$C_6H_5Br + CH_3I + Na_2 = NaBr + NaI + C_6H_5 . CH_3.$$

(2) By the mutual action of benzene (phenyl hydride), and methane (methyl hydride), in the nascent state, as when a mixture of 2 parts of sodium acetate and 1 part of sodium benzoate is subjected to dry distillation:

$$C_6H_6 + CH_4 = C_7H_8 + H_2.$$

It is also produced by distilling toluic acid, $C_8H_{10}O_2$, with lime, which abstracts carbon dioxide:

$$C_8H_{10}O_2 = CO_2 + C_7H_8.$$

It occurs, together with benzene and the other hydrocarbons of the series, in light coal-tar oil, and in the products of the distillation of wood, tolu balsam, dragon's-blood, and other vegetable substances; and, together with many other hydrocarbons, in Rangoon tar or Burmese naphtha.

Toluene is a limpid liquid, smelling like benzene, and having a density of 0·881 at 5° C. (41° F.). It boils at 111° C. (232° F.), and does not solidify at —20° C. (—4° F.). In respect of solubility and solvent power, it is very much like benzene, but dissolves somewhat more readily in alcohol.

When treated with oxidizing agents, it yields benzoic acid, $C_7H_6O_2$, or derivatives thereof; with potassium chromate and sulphuric acid, it yields benzoic acid; and by prolonged boiling with strong nitric acid, nitrobenzoic acid.

Toluene vapor passed through a red-hot porcelain tube is partly resolved into hydrogen gas (with small quantities of methane and ethine), and the following liquid products: (1) Benzene and naphthalene in considerable quantities. (2) A crystallizable hydrocarbon volatilizing at 280° C. (586° F.), and probably consisting of dibenzyl, $C_{14}H_{14}$. (3) A liquid isomeric with the last. (4) A mixture, distilling above 360°, of anthracene with an oily liquid. (5) Chrysene and the last decomposition-products of benzene. The formation of benzene, naphthalene, anthracene, and dibenzyl is represented by the equations:

$$\underset{\text{Toluene.}}{2C_7H_8} = \underset{\text{Dibenzyl.}}{C_{14}H_{14}} + H_2; \qquad \underset{\text{Toluene.}}{2C_7H_8} = \underset{\text{Anthracene.}}{C_{14}H_{10}} + 3H_2.$$

$$\underset{\text{Toluene.}}{4C_7H_8} = \underset{\text{Benzene.}}{3C_6H_6} + \underset{\text{Naphthalene.}}{C_{10}H_8} + 3H_2.$$

Substitution-products of Toluene. — The formula of toluene, $C_6H_5.CH_3$, indicates the existence of two series of substitution-products, according as the replacement of the hydrogen by other radicals takes place in the phenyl atom or benzene residue, or in the methyl atom; thus:

$C_6H_4Cl.CH_3$ Monochlorotoluene.	is isomeric with	$C_6H_5.CH_2Cl$ Benzyl chloride.
$C_6H_4(OH).CH_3$ Cresol.	"	$C_6H_5.CH_2(OH)$ Benzyl alcohol.
$C_6H_4(NH_2).CH_3$ Toluidine.	"	$C_6H_5.CH_2(NH_2)$ Benzylamine.

These isomeric derivatives differ considerably from one another in their properties. Those on the left-hand column, formed by replacement of hydrogen in the benzene residue, are comparatively stable and indifferent compounds, like those derived in like manner from benzene itself; whereas those on the right-hand column, formed by replacement of hydrogen in the methyl atom, are more active bodies, easily exchanging their chlorine, hydroxyl, &c., for other radicals by double decomposition, like the corresponding derivatives of the paraffins (p. 552). Thus benzyl alcohol treated with hydrochloric acid yields benzyl chloride (just as ordinary ethyl alcohol similarly treated yields ethyl chloride); and this compound heated with ammonia yields benzylamine; the chloride is also easily converted into the acetate, cyanide, &c., by treatment with the corresponding potassium salts. In short, these last-mentioned toluene derivatives exhibit reactions exactly like those of the corresponding compounds of the methyl and ethyl series, and may in like manner be supposed to contain an alcohol-radical, C_7H_7, called *benzyl*, or *tolyl*, *e. g.*, benzyl chloride $= C_7H_7.Cl$; benzyl alcohol, $C_7H_7.OH$; benzylamine $= C_7H_7.NH_2$, &c.

Chlorotoluenes.—The action of chlorine on toluene gives rise to a number of substitution-products, differing in constitution according as the reaction takes place at high or at low temperatures. Compounds isomeric with these are also obtained from benzyl alcohol. Of the two monochlorinated compounds whose existence is indicated by theory, viz., monochlorotoluene and benzyl chloride, the first is produced at low, the second at comparatively high temperatures, as when toluene is distilled in a current of chlorine gas, keeping the temperature between 110° and 140° C. (230°–284° F.)

Chlorotoluene boils at 157°–158° C. (314°–316° F.); benzyl chloride at 176°. The former treated with sodium yields toluene.

Of the dichlorinated derivatives of toluene, three isomers may exist, viz.:

$C_6H_3Cl_2 . CH_3$	$C_6H_4Cl . C_2HCl$	$C_6H_5 . CHCl_2$
Dichloro-toluene.	Chlorobenzyl chloride.	Chlorobenzol (so called).

The first does not appear to have been obtained, at least in the pure state. The second is formed by the action of chlorine on benzyl chloride, or on monochlorotoluene; it is a liquid boiling somewhat below 200° C. (392° F.). When treated with alcoholic potash, it easily gives up half its chlorine (that contained in the methyl atom,) but the other half is more obstinately retained. *Chlorobenzol*, or *dichloromethyl-benzene*, is produced by the action of phosphorus pentachloride on benzoic aldehyde or bitter almond oil (C_7H_6O). It is a colorless strongly refracting oil, which boils at 206° C. (403° F.), and when heated to 120°–130° C. (248°–266° F.) with water or aqueous potash, easily gives up the whole of its chlorine in exchange for oxygen, reproducing benzoic aldehyde:

$$\underset{\text{Chlorobenzol.}}{C_6H_5 . CHCl_2} + OH_2 = 2HCl + \underset{\text{Benzoic aldehyde.}}{C_6H_5 . COH}$$

The more highly chlorinated toluenes, $C_7H_5Cl_3$ and $C_7H_4Cl_4$, admit of a still greater number of isomeric modifications; but we cannot here describe them in detail.

The *bromotoluenes* are analogous in composition and mode of formation to the chlorotoluenes, and exhibit corresponding isomeric modifications.

Nitrotoluenes.—Mononitrotoluene, $C_7H_7(NO_2)$, is formed by treating toluene in the cold with fuming nitric acid, and separates on addition of water as a red liquid; but on redistilling this liquid, collecting the portion which passes over below 240° C. (464° F.), and dissolving it in alcohol, it is obtained in white shining crystals, which melt at 54° C. (129° F.), and distil without decomposition at 238° C. (460° F.). By the action of ammonium sulphide it is converted into *amidotoluene*, or *toluidine*, $C_7H_7(NH_2)$. *Dinitrotoluene*, $C_7H_6(NO_2)_2$, and *Trinitrotoluene*, $C_7H_5(NO_2)_3$, are crystalline bodies obtained by treating toluene with hot fuming nitric acid. The former is converted by ammonium sulphide into *nitrotoluidine*, $C_7H_6(NO_2)(NH_2)$.

Xylene, C_8H_{10}, or **Dimethyl-benzene**, $C_6H_4(CH_3)_2$, or **Methyltoluene**, $C_7H_7(CH_3)$. This body is produced synthetically by the action of sodium on a mixture of bromotoluene and methyl iodide:

$$C_6H_4Br . CH_3 + CH_3I + Na_2 = NaBr + NaI + C_6H_4(CH_3)_2.$$

It is contained in light coal-naphtha, and may be prepared by subjecting the least volatile portion of that which has been distilled off in benzene manufactories to fractional distillation, to separate the portion which boils at about 141° C. (286° F.); this portion is shaken up with oil of vitriol containing a little fuming sulphuric acid, which dissolves the xylene as xylene-sulphuric acid, $C_8H_{10}SO_3$; this compound is decomposed by dry distillation; and the xylene which passes over is purified by washing, drying, and distillation.

Xylene is a colorless liquid of specific gravity 0·86 at 19° C. (66° F.), and boiling at 139° C. (282° F.). When passed in the state of vapor through a red-hot tube, it is resolved into a mixture of several hydrocarbons, among which are benzene, toluene, styrolene, C_8H_8, naphthalene, anthracene, and its higher homologues. The formation of some of these products is represented by the following equations:

$$\underset{\text{Xylene.}}{C_8H_{10}} - H_2 = \underset{\text{Styrolene.}}{C_8H_8}$$

$$3\underset{\text{Xylene.}}{C_8H_{10}} - 3H_2 = 2\underset{\text{Toluene.}}{C_7H_8} + \underset{\text{Styrolene.}}{C_{10}H_8}$$

$$2\underset{\text{Toluene.}}{C_7H_8} - 3H_2 = \underset{\text{Anthracene.}}{C_{14}H_{10}}$$

Xylene oxidized with a mixture of *sulphuric acid* and *potassium chromate* is converted into terephthalic acid, $C_8H_6O_4$; dilute *nitric acid* converts it into the intermediate product, toluic acid, $C_8H_8O_2$:

$$C_8H_{10} + O_3 = OH_2 + C_8H_8O_2$$
$$C_8H_{10} + O_6 = 2OH_2 + C_8H_6O_4.$$

Chlorine and *bromine* act upon xylene in the same manner as upon toluene, forming substitution derivatives, which are susceptible of a larger number of isomeric modifications than those of toluene, inasmuch as xylene contains two atoms of methyl, whereas toluene contains only one; but they have not been very minutely examined.

There are three *nitroxylenes*, containing respectively $C_8H_9(NO_2)$, $C_8H_8(NO_2)_2$, and $C_8H_7(NO_2)_3$. The first and second are produced by the action of cold fuming nitric acid upon xylene. *Mononitroxylene* is a heavy oil, converted by reducing agents into xylidine, $C_8H_7(NH_2)$; *dinitroxylene* is a solid, which separates from dilute alcohol in shining crystals, melting at 93°. *Trinitroxylene*, formed by treating xylene with a mixture of nitric and sulphuric acids, is a crystalline body, converted by reducing agents into dinitroxylidine, $C_8H(NO_2)_2(NH_2)$.

Ethyl-benzene, $C_6H_5(C_2H_5)$, isomeric with xylene, is produced by the action of sodium on a mixture of monobromo-benzene and ethyl bromide. It is a colorless, mobile liquid, very much like toluene, and boiling at 133° C. (271° F.). By oxidation with potassium chromate and sulphuric acid it yields benzoic acid. It is slowly attacked by bromine, forming *monobrom-ethylbenzene*, $C_8H_4Br(C_2H_5)$, which is a liquid boiling at 200° C. (392° F.); whereas monobromo-xylene boils at about 203° C. (397° F.). Heated with bromine to 100°, it yields more highly brominated compounds, which are also liquid. There are three nitro-ethyl benzenes, which are all liquid at ordinary temperatures.

Isomeric Hydrocarbons, C_9H_{12}. — This formula includes the three following isomeric bodies:

$C_6H_3(CH_3)_3$	$C_6H_4(CA_3)(C_2H_5)$	$C_6H_5(C_3H_7)$
Trimethyl-benzene.	Methyl-ethyl-benzene.	Propyl-benzene.

The first two have been prepared synthetically.

Trimethyl-benzene, $C_6H_3(CH_3)_3$, also called *Coal-tar Cumene*, and *Pseudocumene*. — This hydrocarbon is produced by the action of sodium on a mixture of monobromoxylene and methyl-iodide:

$$C_6H_3Br(CH_3)_2 + CH_3I + Na_2 = NaBr + NaI + C_6H_3(CH_3)_3.$$

From coal-tar oil it is obtained by heating the portion which passes over in fractional distillation near its boiling-point, with strong sulphuric acid, decomposing the resulting cumene-sulphuric acid by distillation, and subjecting the product to fractional distillation. It boils at 166° C. (331° F.). The same hydrocarbon exists in Burmese naphtha. With *bromine* it yields monobromotrimethylbenzene, $C_9H_{11}Br$, which crystallizes from alcohol in large white laminæ, melting at 73° C. (163° F.). The dibrominated com-

pound appears to be liquid. No nitro-derivatives of pseudo-cumene have yet been obtained.

Methyl-ethyl-benzene, or Ethyl-toluene, $C_6H_4(CH_3)(C_2H_5)$, is prepared by the action of sodium on a mixture of monobromotoluene and ethyl bromide. It boils at 159° C. (318° F.), and when oxidized with potassium chromate and sulphuric acid, yields terephthalic acid.

Propyl-benzene, or Cumene, $C_6H_5(C_3H_7)$. — This hydrocarbon is related to cuminic acid, $C_{10}H_{12}O_2$, in the same manner as benzene to benzoic acid, and is produced by distilling cuminic acid with excess of baryta:

$$C_{10}H_{12}O_2 = CO_2 + C_9H_{12}.$$

It is also produced from phorone ($C_{10}H_{14}O$) by the dehydrating action of phosphoric oxide:

$$C_{10}H_{14}O - OH_2 = C_9H_{12}.$$

Cumene boils at 152°–153° C. (305°–7° F.). By treatment with potassium chromate and sulphuric acid, or by prolonged boiling with dilute nitric acid, it yields benzoic acid. When boiled with strong nitric acid, it is converted into nitro-benzoic acid. With *chlorine* it yields, according to Fittig,* a viscid, non-distillable oil, probably consisting of $C_9H_{12}Cl_6$. Cumene dissolves in fuming nitric acid, and water added to the solution throws down nitrocumene, $C_9H_{11}(NO_2)$, as a yellow oil, which by reduction yields amidocumene or cumidine, $C_9H_{11}(NH_2)$.

Mesitylene. — This compound, likewise isomeric with cumene, is produced in small quantity by distilling acetone made up into a paste with sand, with strong sulphuric acid, and is purified by repeated fractional distillation, finally over sodium. It is a liquid which boils at 163° C. (325° F.), and when oxidized with potassium chromate and sulphuric acid yields acetic acid, but no benzoic acid. Hence it appears to have a constitution totally different from that of the aromatic hydrocarbons. Treated with cold fuming nitric acid, not in excess, it yields liquid nitromesitylene, $C_9H_{11}(NO_2)$; when dropped into cooled fuming nitric acid it forms crystallizable dinitromesitylene, $C_9H_{10}(NO_2)_2$; and when treated in like manner with a mixture of oil of vitriol and fuming nitric acid, it is converted into trinitromesitylene, $C_9H_9(NO_2)_3$. These three nitro-compounds, subjected to the action of reducing agents, yield the three amido-compounds, amido-mesitylene, or mesidine, $C_9H_{11}(NH_2)$, nitromesidine, $C_9H_{10}(NO_2)(NH_2)$, and dinitromesidine, $C_9H_9(NO_2)_2(NH_2)$.

Isomeric Hydrocarbons, $C_{10}H_{14}$. — Theory indicates the existence of five bodies of this group, viz., tetramethyl-benzene, dimethyl-ethyl-benzene, diethyl-benzene, methyl-propyl-benzene, and quartyl-benzene. Of these the second only has been prepared synthetically. Tetramethyl-benzene probably occurs amongst the products of the destructive distillation of coal; but it has not been isolated. Cymene, a hydrocarbon existing in various essential oils, is probably methyl-propyl-benzene.

Dimethyl-ethyl-benzene, or Ethyl-xylene, $C_6H_3(CH_3)_2(C_2H_5)$, is prepared by treating a mixture of monobromoxylene and ethyl-bromide with sodium. It boils at 183°–184° C. (361°–363° F.). With *bromine* it forms heavy oily compounds, and with a large excess of bromine a crystalline compound. By prolonged warming with a mixture of fuming nitric and sulphuric acids, it yields a crystalline trinitro-derivative, melting at 119° C. (246° F.).

Cymene. — This name is applied to two isomeric hydrocarbons, $C_{10}H_{14}$, agreeing in composition, but differing in some of their physical and chemical properties.

* Ann. Ch. Pharm. cxii. 314.

a. Cymene.—This hydrocarbon exists, together with cuminic aldehyde, in the essential oil of Roman cumin (*Cuminum cyminum*), and may be obtained by distilling that oil with alcoholic solution of potash, the cuminic aldehyde being converted into cymene, and the cymene which exists ready-formed in the oil passing over at the same time:

$3C_{10}H_{12}O$	+	K_2O	=	$2C_{10}H_{11}KO_2$	+	$C_{10}H_{14}$
Cuminic aldehyde.		Potassium oxide.		Potassium cuminate.		Cymene.

a cymene is a colorless, strongly refracting oil, of sp. gr. 0·86 at 14° C. (57° F.), boiling at 175°–178° C. (347°–352° F.). By prolonged boiling with dilute nitric acid it is converted into toluic acid, $C_7H_7(CO_2H)$; with stronger nitric acid it yields nitrotoluic acid; and by boiling with potassium chromate and sulphuric acid, it forms terephthalic acid, $C_8H_{10}O_4=C_6H_4(CO_2)H_2$. According to Sieveking, it unites with chlorine and bromine, forming the liquid compounds $C_{10}H_{14}Cl_2$ and $C_{10}H_{14}Br_2$; according to Fittig and Ferber, it forms only substitution-products. — Cold fuming nitric acid converts it into liquid nitrocymene, $C_{10}H_{13}(NO_2)$, which is converted by reducing agents into cymidine, $C_{10}H_{13}(NH_2)$. By prolonged heating with a mixture of nitric and sulphuric acids, it is converted into dinitrocymene, $C_{10}H_{12}(NO_2)_2$, which crystallizes from alcohol in long needles or laminæ, melting at 69·5° C. (157° F.); by still further treatment (for several days) with the mixed acids, it appears to yield crystalline trinitrocymene, melting at 107° C.

β. Cymene is obtained by heating camphor in a retort with zinc chloride:

$C_{10}H_{16}$	—	OH_2	=	$C_{10}H_{14}$
Camphor.				Cymene.

The product is purified from lighter hydrocarbons by fractional distillation.

β cymene boils at 177°–179° C. (351°–356° F.). It does not yield terephthalic acid by oxidation. With bromine it easily forms the crystalline compound $C_{10}H_{12}Br_2$. Nitric acid acts upon it in the same manner as on *a* cymene; but *β* dinitrocymene crystallizes in thin plates melting at 90°, and is easily converted into *β* trinitrocymene, which crystallizes from alcohol in short thin prisms melting at 112·5° C. (234° F.).

Amyl-benzene, $C_{11}H_{16}=C_6H_5(C_5H_{11})$.—This, which is the only known aromatic hydrocarbon containing 11 carbon atoms, is produced by the action of sodium on a mixture of bromobenzene and amyl bromide diluted with benzene.* It has a specific gravity of 0·86 at 12° C. (54° F.), and boils at 195° C. (383° F.). With chlorine it yields viscid products; with nitric acid in the cold a liquid, non-distillable mononitro-derivate; at higher temperatures, dinitro-amyl-benzene.

Sixth Series, C_nH_{2n-8}.

The only known hydrocarbons of this series are *phenylene*, C_6H_4, and *cinnamene*, or *styrolene*, C_8H_8, with its isomer, metacinnamene.

Of *phenylene* very little is known. A liquid having the composition C_6H_4, and boiling at 91° C. (196° F.), was found by Church† among the products of the decomposition of monochloro-benzene by sodium amalgam. It is probably also formed, together with benzene, when diphenyl, $C_{12}H_{10}$,

* *Fittig* and *Tollens*, Ann. Ch. Pharm. cxxxi. 313.
† Journal of the Chemical Society, xvi. 76.

is passed through a red-hot tube, but is subsequently converted into the polymeric body, chrysene:*

$$\underset{\text{Diphenyl.}}{C_{12}H_{10}} = \underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Phenylene.}}{C_6H_4}; \text{ and } 3C_6H_4 = \underset{\text{Chrysene.}}{C_{18}H_{12}}.$$

Cinnamene, or **Styrolene**, C_8H_8, is produced—1. Synthetically: *α.* By passing a mixture of benzene-vapor and ethine, or ethene, through a red-hot tube:

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Ethine.}}{C_2H_2} = \underset{\text{Cinnamene.}}{C_8H_8}; \qquad \underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Ethene.}}{C_2H_4} = \underset{\text{Cinnamene.}}{C_8H_8} + H_2$$

The second method yields it in larger quantity than the first.

β. In like manner, together with benzene, from diphenyl and ethene:

$$C_{12}H_{10} + C_2H_4 = C_8H_8 + C_6H_6.$$

2. In the decomposition of xylene which takes place when the vapor of that compound is passed through a red-hot tube: $C_8H_{10} = C_8H_8 + H_2$ (p. 497).

3. By distilling cinnamic acid with baryta, which removes carbon dioxide:

$$C_9H_8O_2 = CO_2 + C_8H_8.$$

4. Cinnamene is contained in liquid storax, and may be separated by distilling the balsam with water containing a little sodium carbonate, to retain cinnamic acid.

Cinnamene is a very mobile, colorless oil of specific gravity 0·924. It boils at 145° C. (293° F.), and does not solidify at —20° C. (68° F.). When heated to 200° C. (392° F.) in a sealed tube, it is converted into a white, transparent, highly refractive, solid substance, called *metacinnamene* or *metastyrolene*. This substance, when heated in a small retort, yields a distillate of pure liquid cinnamene.†

A mixture of cinnamene vapor and ethene passed through a red-hot tube yields large quantities of benzene and naphthalene. The first is produced from the cinnamene by abstraction of C_2H_2; the second according to the equation:

$$C_8H_8 + C_2H_4 = C_{10}H_8 + 2H_2.$$

A mixture of cinnamene and benzene vapors, passed through a red-hot porcelain tube, yields anthracene, $C_{14}H_{10}$, together with small quantities of other products:

$$C_8H_8 + C_6H_6 = C_{14}H_{10} + 2H_2.$$

Cinnamene acts with chlorine and bromine like a bivalent radical, forming the compounds $C_8H_8Cl_2$ and $C_8H_8Br_2$, which, when treated with alcoholic potash, give up HCl and HBr (like the corresponding ethene-compounds), leaving chloro-cinnamene, C_8H_7Cl, and bromo-cinnamene, C_8B_7Br. According to Laurent, cinnamene yields with chlorine a hexchloride of dichlorocinnamene, $C_8H_6Cl_2.Cl_6$; if this be correct, cinnamene must be regarded as a sexvalent radical. — Metacinnamene is also acted upon by bromine, but with considerable difficulty. — Both cinnamene and metacinnamene

* *Berthelot*, Jahresbericht für Chemie, 1866, p. 544.

† It was formerly supposed that cinnamene prepared from cinnamic acid was not converted by heat into a solid modification, like styrolene from storax: hence the two were regarded as isomeric, not identical; but later researches have shown that pure cinnamene from cinnamic acid is likewise convertible into solid metacinnamene.

treated with fuming nitric acid yield mononitrated derivatives, $C_8H_7(NO_2)$: that obtained from cinnamene is crystalline; that from metacinnamene amorphous.

Seventh Series, C_nH_{2n-10}.

The only known hydrocarbon belonging to this series is one containing $C_{26}H_{42}$, which is formed by dehydration of cholesterin, $C_{26}H_{44}O$ (a crystalline compound contained in bile and biliary calculi). It has been but little examined.

Another member of the same series, $C_{10}H_{10}$, might perhaps be formed by heating bromocinnamene with sodium ethylate ($C_8H_7Br+C_2H_5NaO=NaBr+OH_2+C_{10}H_{10}$.)

Eighth Series, C_nH_{2n-12}.

Of this series, also, only one member is known with certainty, namely, *naphthalene*, $C_{10}H_8$, produced in the distillation of coal. According to Chancel, two hydrocarbons, isomeric or polymeric with this body, are formed in the dry distillation of calcium benzoate; but they have not been much studied.

Naphthalene, $C_{10}H_8$. — This hydrocarbon is produced, as already observed, in the decomposition of toluene, xylene, and cumene at a red heat; also by passing vapor of benzene, cinnamene, chrysene, or anthracene through a red-hot tube. It is formed in large quantities as a by-product in the preparation of coal-gas, its production doubtless arising from reactions similar to those just mentioned. When the last portion of the volatile oily product which passes over in the distillation of coal-tar, is collected apart and left to stand, a quantity of solid crystalline matter separates, which is principally naphthalene. An additional quantity may be obtained by pushing the distillation until the contents of the vessel begin to char; the naphthalene then condenses in the solid state, but dark-colored and very impure. By simple sublimation, once or twice repeated, it is obtained perfectly white. In this state naphthalene forms large, colorless, transparent, brilliant, crystalline plates, exhaling a faint and peculiar odor, which has been compared to that of the narcissus. Naphthalene melts at 80° C. (176° F.) to a clear, colorless liquid, which crystallizes on cooling: it boils at 212° C. (414° F.), and evolves a vapor whose density is 4·528. When strongly heated in the air, it inflames and burns with a red and very smoky light. It is insoluble in cold water, but soluble to a slight degree at the boiling temperature; alcohol and ether dissolve it easily; a hot saturated alcoholic solution deposits fine iridescent crystals on cooling.

Naphthalene dissolves in warm strong *sulphuric acid*, forming two crystalline acids: sulphonaphthalic acid, $C_{10}H_8SO_3$, and disulphonaphthalic acid, $C_{10}H_8S_2O_6$, both of which form soluble barium salts.

Naphthalene unites directly with 4 atoms of *bromine* and *chlorine*, forming the compounds $C_{10}H_8Cl_4$ and $C_{10}H_8Br_4$. It also forms a great number of substitution-products with these elements, bromine being capable of replacing from 1 to 4, and chlorine from 1 to 8 atoms of hydrogen in naphthalene; there are also several derivatives containing both bromine and chlorine, *e. g.*, $C_{10}H_3Br_2Cl_3$. Many of these substitution-derivatives are susceptible of isomeric modifications differing from one another in their physical properties. The chloro- and bromo-naphthalenes are capable, like naphthalene itself, of uniting with 4 atoms of bromine or chlorine, and with 2

molecules of hydrochloric or hydrobromic acid, forming such compounds as $C_{10}H_6Cl_2 . Cl_4$, $C_{10}H_4Br_2Cl_2 . 2HCl$, &c.*

With strong *nitric acid*, naphthalene yields the three substitution-products, $C_{10}H_7(NO_2)$, $C_{10}H_6(NO_2)_2$, and $C_{10}H_5(NO_2)_3$, all of which are white crystalline solids. The first is converted by reducing agents into amidonaphthalene, naphthalidine, or naphthylamine, $C_{10}H_7(NH_2)$.

Ninth Series, C_nH_{2n-14}.

Two members of this series are known, viz., *diphenyl*, $C_{12}H_{10}$, and *dibenzyl*, $C_{14}H_{14}$; they are so called because their molecules are the doubles of the hypothetical monatomic radicals, phenyl, C_6H_5, and benzyl, C_7H_7.

Diphenyl, $C_{12}H_{10}$, is produced: (1) as already observed, by passing benzene vapor through a red-hot tube: $2C_6H_6 = C_{12}H_{10} + H_2$. (2) By the action of sodium on phenyl bromide or monobromobenzene:

$$2C_6H_5Br + Na_2 = 2NaBr + C_{12}H_{10}.$$

(3) Together with other products, by the action of alcoholic potash on nitrate of diazobenzene:†

$2C_6H_4N_2$	+	C_2H_6O	=	$C_{12}H_{10}$	+	C_2H_4O	+	$2N_2$
Diazobenzene.		Alcohol.		Diphenyl.		Aldehyde.		

Diphenyl appears also to be one of the constituents of crude anthracene (p. 504), and passes over in the distillation of that substance, at about 260° C. (500° F.)

Diphenyl crystallizes from alcohol in iridescent nacreous scales, which melt at about 60° C. (140° F.), sublime at a higher temperature, and boil at about 240° C. (464° F.). It is converted by bromine into dibromodiphenyl, $C_{12}H_8Br_2$, and by fuming nitric acid into dinitro-diphenyl, $C_{12}H_8(NO_2)_2$. The latter is converted by hydrogen sulphide into diamido-diphenyl or benzidine, $C_{12}H_8(NH_2)_2$, a crystalline base, which, when treated with nitrous acid, yields the nitrate of tetrazodiphenyl or diazobenzidine:

$C_{12}H_{12}N_4$	+	$2NHO_2$	=	$C_{12}H_6N_4$		$4OH_2$.
Diamido-diphenyl.		Nitrous acid.		Tetrazo-diphenyl.		

Dibenzyl, $C_{14}H_{14}$, is produced by heating benzyl chloride, C_7H_7Cl, or benzylidene bromide, $C_7H_6Br_2$ (a product of the action of phosphorus pentabromide on bitter-almond oil), with sodium. It is a crystalline solid, insoluble in water, but soluble in alcohol and ether; melts at about 52° C. (126° F.), and distils without decomposition at 284° C. (543° F.). When treated with bromine and water, it yields the substitution-products, $C_{14}H_{13}Br$, $C_{14}H_{12}Br_2$, $C_{14}H_{11}Br_3$, and $C_{14}H_8Br_6$, all of which are crystalline at ordinary temperatures, except the first, which is an oil solidifying when cooled below 0°. Dibenzyl also unites directly with *bromine*, forming the crystalline compound $C_{14}H_{14}Br_2$. Fuming *nitric acid* converts it into dinitro-dibenzyl, $C_{14}H_{12}(NO_2)_2$, which crystallizes in needles, and is converted by reducing agents into the corresponding amido-compound, $C_{14}H_{12}(NH_2)_2$.

* See Watts's Dictionary of Chemistry, vol. iv. p. 6.
† Griess, Phil. Trans. 1864, part iii. p. 692.

Tenth Series, C_nH_{2n-16}.

Of this series only one member has hitherto been obtained, viz., *stilbene*, $C_{14}H_{12}$, which is formed, together with other products, by heating benzylidene sulphide:

$$\underset{\text{Benzylidene sulphide.}}{8C_7H_6S} = \underset{\text{Stilbene.}}{2C_{14}H_{12}} + \underset{\text{Thionessal.}}{C_{26}H_{18}S} + 2CS_2 + 3SH_2$$

It crystallizes in colorless plates having a mother-of-pearl lustre, melts above 100°, and boils at 292° C. (558° F.). It forms substitution-products with chlorine, bromine, and nitric acid, and unites directly with chlorine, forming the compound $C_{14}H_{12}Cl_2$.

Eleventh Series, C_nH_{2n-18}.

Anthracene, or Paranaphthalene, $C_{14}H_{10}$, is produced: (1) By passing a mixture of benzene with ethene gas or cinnamene vapor, or of diphenyl or chrysene vapor with ethene gas, through a red-hot porcelain tube; also by exposing a mixture of benzene and naphthalene vapor to a white heat:

$$\underset{\text{Benzene.}}{2C_6H_6} + \underset{\text{Ethene.}}{C_2H_4} = 3H_2 + \underset{\text{Anthracene.}}{C_{14}H_{10}}$$

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Cinnamene.}}{C_8H_8} = 2H_2 + \underset{\text{Anthracene.}}{C_{14}H_{10}}$$

$$\underset{\text{Diphenyl.}}{C_{12}H_{10}} + \underset{\text{Ethene.}}{C_2H_4} = H_2 + \underset{\text{Anthracene.}}{C_{14}H_{12}}$$

$$\underset{\text{Chrysene.}}{C_{18}H_{12}} + \underset{\text{Ethene.}}{C_2H_4} = \underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Anthracene.}}{C_{74}H_{10}}$$

$$\underset{\text{Naphthalene.}}{C_{10}H_8} + \underset{\text{Benzene.}}{3C_6H_6} = 3H_2 + \underset{\text{Anthracene.}}{2C_{14}H_{10}}$$

Also when toluene, xylene, or cumene is passed through a red-hot tube (pp. 496, 497).

Anthracene is produced in the dry distillation of coal, bituminous shale, and wood, and is contained in the last heavy and semifluid portions of the tar, at first together with naphthalene, finally with chrysene. A commercial product of this kind, used as a lubricator for machinery, is yellow, soft, somewhat like palm-oil, and contains anthracene, together with several of its homologues and other hydrocarbons. To obtain pure anthracene, the crude commercial product is distilled from an iron retort, the first and last portions of the distillate being rejected, and the intermediate portion crystallized either from alcohol or from coal-oils boiling between 100° and 120° C. (212°–248° F.).

Anthracene forms small colorless micaceous laminæ, of sp. gr. 1·147, melting at about 213° C. (415° F.), subliming slowly at 100°, more quickly at a stronger heat, and boiling between 220° and 230° C. (428°–446° F.). It is insoluble in water, but dissolves easily in boiling alcohol, more abundantly in ether, benzene, and volatile oils, especially oil of turpentine. It forms substitution-products with *bromine* and *chlorine*. Dibromanthracene unites with bromine, forming the compound $C_{14}H_8Br_2 . Br_2$, and chloranthracene forms a hydrochloride containing $C_{14}H_7Cl . HCl$.

Anthracene, boiled with *nitric acid* for some days, is converted into *oxan-*

thracene, $C_{14}H_8O_4$, or $C_{14}H_8O \cdot O$, and if fuming nitric acid be added from time to time, *dinitroxanthracene*, $C_{14}H_6(NO_2)_2O_2$, is obtained.

Pyrene, a hydrocarbon obtained by Laurent, together with chrysene, from the least volatile portion of coal-tar, appears to be identical with anthracene.

Crude anthracene contains also several hydrocarbons homologous with anthracene, and less volatile than anthracene itself; among others, *methyl-anthracene*, $C_{15}H_{12}$, or $C_{14}H_9(CH_3)$, which is identical with the paranaphthalene of Dumas, and *tetramethyl-anthracene*, or *retene*, $C_{18}H_{18}$, or $C_{14}H_6(CH_3)_4$.

Retene, which is polymeric with benzene, likewise occurs in thin unctuous scales on fossil pine-stems in beds of peat and lignite in Denmark and other localities. It is produced also in the dry distillation of very resinous fir and pine-wood, passing over together with the heavy tar-oil, and separating in scales like paraffin. It is soluble in warm alcohol and ether, and dissolves easily in oils both fixed and volatile; sulphuric acid converts it into *disulphoretic acid*, $C_{18}H_{18}S_2O_6$.

Twelfth Series, C_nH_{2n-24}.

Chrysene, $C_{18}H_{12}$, is produced, together with benzene, by heating diphenyl for an hour in a sealed tube filled with hydrogen, the diphenyl being probably resolved in the first instance into benzene and phenylene, which latter is then polymerized into chrysene:

$$\underset{\text{Diphenyl.}}{C_{12}H_{10}} = \underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Phenylene.}}{C_6H_4}; \text{ and } 3\underset{\text{Phenylene.}}{C_6H_4} = \underset{\text{Chrysene.}}{C_{18}H_{12}}.$$

Chrysene is also found, together with benzerythrene (p. 493), in the last product obtained by the distillation of crude anthracene, and in the residue left in the retort; in larger quantity also in the last products of the distillation of pitch. Laurent likewise obtained it together with pyrene (anthracene) by the dry distillation of fats and resins. Pure chrysene has a fine yellow color. It is insoluble in alcohol, nearly insoluble in ether, and is deposited from boiling oil of turpentine in yellow crystalline flakes.

APPENDIX TO HYDROCARBONS.

Petroleum, Naphtha, and other allied Substances.

Pit-coal, lignite or *brown coal, jet, bitumen* of various kinds, *petroleum* or *rock-oil*, and *naphtha*, and a few other allied substances more rarely met with, are looked upon as products of the decomposition of organic matter, especially vegetable matter, beneath the surface of the earth, in situations where the conditions of contact with water, and nearly total exclusion of atmospheric air, are fulfilled. Deposited at the bottom of seas, lakes, or rivers, and subsequently covered up by accumulations of clay and sand hereafter destined to become shale and gritstone, the organic tissue undergoes a kind of fermentation by which the bodies in question, or certain of them, are slowly produced. Carbon dioxide and marsh-gas are bye-products of the reaction; hence their frequent disengagement, the first from beds of lignite, and the second from the further advanced and more perfect coal.

The vegetable origin of coal has been placed beyond doubt by microscopic research; vegetable structure can be thus detected even in the most

massive and perfect varieties of coal when cut into thin slices. In coal of inferior quality, much mixed with earthy matter, it is evident to the eye. The leaves of ferns, reeds, and other succulent plants, more or less resembling those of the tropics, are found in a compressed state between the layers of shale or slaty clay, preserved in the most beautiful manner, but entirely converted into bituminous coal. The coal-mines of Europe, and particularly those of our own country, furnish an almost complete fossil flora — a history of many of the now lost species which once decorated the surface of the earth.

In the lignites the woody structure is much more obvious. Beds of this material are found in very many of the newer strata, above the true coal, to which they are consequently posterior. As an article of fuel, brown coal is of comparatively small value: it resembles peat, giving but little flame, and emitting a disagreeable pungent smell.

Jet, used for making black ornaments, is a variety of lignite.

The true bitumens are destitute of organic structure: they appear to have arisen from coal or lignite by the action of subterranean heat; and very closely resemble some of the products yielded by the destructive distillation of those bodies. They are very numerous, and have yet been but imperfectly studied.

1. *Mineral pitch*, or *compact bitumen*, the *asphaltum* or *Jew's pitch* of some authors.—This substance occurs abundantly in many parts of the world—as in the neighborhood of the Dead Sea in Judea; in Trinidad, in the famous *pitch lake*, and elsewhere. It generally resembles in aspect common pitch, being a little heavier than water, easily melted, very inflammable, and burning with a red, smoky flame. It consists principally of a substance, called by Bossingault *asphaltene*, composed of $C_{20}H_{32}O_3$. It is worthy of remark, that Laurent found paranaphthalene in a native mineral pitch.

2. *Mineral tar* seems to be essentially a solution of asphaltene in an oily fluid called *petrolene*. This liquid has a pale-yellow color, and peculiar odor; it is lighter than water, and very combustible, and has a high boiling-point. It has the same composition as the oils of turpentine and lemon-peel--namely, $C_{10}H_{16}$. Asphaltene contains, consequently, the elements of petrolene, together with a quantity of oxygen, and probably arises from the oxidation of that substance.

3. *Elastic bitumen; mineral caoutchouc.* — This curious substance has only been found in three places: in a lead-mine at Castleton, in Derbyshire; at Montrelais, in France; and in the State of Massachusetts. In the two latter localities it occurs in the coal series. It is fusible, and in many respects resembles the other bitumens.

Under the names *petroleum* or *rock-oil* and *naphtha* are arranged various mineral oils which are observed in many places to issue from the earth, often in considerable abundance. There is every reason to suppose that these owe their origin to the action of internal heat upon beds of coal, as they are usually found in connection with such. The term *naphtha* is given to the thinner and purer varieties of rock-oil, which are sometimes nearly colorless; the darker and more viscid liquids bear the name of *petroleum*.

Some of the most noted localities of these substances are the following: The north-west side of the Caspian Sea, near Baku, where beds of marl are found saturated with naphtha. Wells are sunk to the depth of about 30 feet, in which naphtha and water collect, and are easily separated. In some parts of this district so much combustible gas or vapor rises from the ground, that, when set on fire, it continues burning, and even affords heat for economical purposes. A large quantity of an impure variety of petroleum comes from the Birman territory in the East Indies: the country consists of sandy clay, resting on a series of alternate strata of sandstone and

shale. Beneath these occurs a bed of pale-blue shale loaded with petroleum, which lies immediately on coal. A petroleum-spring exists at Colebrook Dale, in Shropshire, and immense quantities come now from Canada, Pennsylvania, and other parts of North America. The sea near the Cape de Verd Islands has been seen covered with a film of rock-oil. Fine specimens of naphtha are furnished by Italy, where it occurs in several places.

In proof of the origin attributed to these substances, an old experiment of Reichenbach may be cited, who, by distilling with water about 100 lbs. of pit-coal, obtained nearly 2 ounces of an oily liquid, exactly resembling the natural naphtha of Amiano, in Italy. The manufacture of such products (paraffin oils) by distilling Boghead and other kinds of coal at a low red heat, is now conducted on a very large scale (p. 476).

The variations of color and consistence in different specimens of rock-oil depend in great measure upon the presence of pitchy and fatty substances dissolved in the more fluid oil.

The boiling point of rock-oil varies from about 80° to 326°. A thermometer inserted into a retort in which the oil is undergoing distillation, never shows for any length of time a constant temperature: hence it is inferred to be a mixture of several different substances. Neither do the different varieties of naphtha give similar results on analysis: they are all, however, hydrocarbons, chiefly paraffins, with smaller quantities of olefines and aromatic hydrocarbons. The use of these substances in the places where they abound is tolerably extensive; they often serve the inhabitants for fuel, light, &c. To the chemist, pure naphtha is valuable, as offering facilities for the preservation of the more oxidable metals, as potassium and sodium.

Among the several naphthas, the *Burmese naphtha* (Rangoon tar) has been more particularly examined by De la Rue and Müller. It consists principally of liquid homologues of marsh-gas, including solid paraffin, associated with small quantities of hydrocarbons of the benzene series, and hydrocarbons analogous to colophene. American petroleum, which has a similar composition, but contains a larger proportion of the homologues of marsh-gas, has been investigated chiefly by Pelouze and Cahours (p. 476).

Retinite, or *Retinasphalt*, is a kind of fossil resin met with in brown coal: it has a yellow or reddish color, is fusible and inflammable, and readily dissolved in great part by alcohol. The soluble portion is called *retinic acid*. *Hatchetin* is a somewhat similar substance met with in mineral coal at Merthyr Tydvil, and also near Loch Fyne, in Scotland. *Idrialin* is found associated with native cinnabar, and is extracted from the ore by oil of turpentine, in which it dissolves. It is a white, crystalline substance, scarcely volatile without decomposition, but slightly soluble in alcohol and ether, and composed of $C_{42}H_{28}O$: it is generally associated with a hydrocarbon, *idryl*, which contains $C_{21}H_{14}$.

Ozocerite, or *fossil wax*, is found in Moldavia, in a layer of bituminous shale: it is brownish, and has a somewhat pearly appearance: it is fusible below 100°, and soluble with difficulty in alcohol and ether, but easily in oil of turpentine. It appears to contain more than one definite principle.

Nefte-degil, a substance resembling the former, occurs in immense quantities in the vicinity of the Caspian Sea. Another compound of the same kind is found in still larger quantities at Baku, and is called *Kir*.

ALCOHOLS AND ETHERS.

THE term alcohol, originally limited to one substance, viz., spirit of wine, is now applied to a large number of organic compounds, many of which, in their external characters, exhibit but little resemblance to ordinary alcohol. They are all, however, analogously constituted, having the composition of saturated hydrocarbons, in which one or more of the hydrogen-atoms are replaced by hydroxyl: they may, therefore, also be regarded as compounds of hydroxyl with univalent or multivalent hydrocarbon radicals, hence called *alcohol radicals*. Thus, from propane, C_3H_8, are derived the three alcohols,

$C_3H_7(OH)$	$(C_3H_6)''(OH)_2$	$(C_3H_5)'''(OH)_3$
Propyl alcohol.	Propene alcohol.	Propenyl alcohol.

Alcohols are accordingly classed as *monatomic*, *diatomic*, *triatomic*, &c., or, generally, as *monatomic* and *polyatomic*, according to the number of equivalents of hydroxyl which they contain; or according to the equivalent value of their hydrocarbon radicals.

The replacement, partial or total, of the hydroxyl in an alcohol by chlorine, bromine, iodine, or fluorine, gives rise to *haloïd ethers;* thus:

From $C_3H_7(OH)$ are derived C_3H_7Cl, C_3H_7Br, &c.
" $C_3H_6(OH)_2$ " C_3H_6ClOH, $C_3H_6Cl_2$, &c.
" $(C_3H_5)(OH)_3$ " $C_3H_5Cl(OH)_2$, $C_3H_5Cl_2(OH)$, $C_3H_5Cl_3$, $C_3H_5Br_2Cl_3$, &c.

These substitutions are effected by treating the alcohols with the chlorides, bromides, and iodides of hydrogen or phosphorus; thus:

$C_2H_5(OH)$	+	HCl	=	$H(OH)$	+	C_2H_5Cl
Ethyl alcohol.		Hydrogen chloride.		Water.		Ethyl chloride.
$3C_2H_5(OH)$	+	PCl_3	=	$P(OH)_3$	+	$3C_2H_5Cl$
Ethyl alcohol.		Phosphorous chloride.		Phosphorous acid.		Ethyl chloride.
$3C_2H_5(OH)$	+	$POCl_3$	=	$PO(OH)_3$	+	$3C_2H_5Cl$
Ethyl alcohol.		Phosphorous oxychloride.		Phosphorous acid.		Ethyl chloride.

Instead of the bromides and iodides of phosphorus, the elements phosphorus and bromine or iodine, in the proportions required to form them, are often used in these processes.

These haloïd ethers are also formed in many instances by direct substitution of chlorine, bromine, &c., for hydrogen in saturated hydrocarbons, as explained in the preceding pages.

The treatment of the haloïd ethers with caustic aqueous alkalies gives rise to a substitution opposite to that exhibited in the above equations, reconverting the ethers into alcohols, *e. g.:*

$$C_2H_5Cl + KOH = KCl + C_2H_5(OH).$$

The replacement of the hydroxyl in an alcohol by the corresponding

radicals, potassoxyl, OK, methoxyl, OCH_3, ethoxyl, OC_2H_5, &c. (p. 237), — or of the hydrogen in the hydroxyl by potassium, methyl, ethyl, &c., — gives rise to *oxygen ethers;* thus:

$C_2H_5(OH)$	yields	$C_2H_5(OK)$	$C_2H_5(OCH_3)$	$C_2H_5(OC_2H_5)$
Ethyl alcohol.		Potassium ethylate.	Methyl ethylate.	Ethyl ethylate.
$C_2H_4(OH)_2$	"	$C_2H_4(OH)(OC_2H_5)$		$C_2H_4(OC_2H_5)_2$
Ethene alcohol.		Monethylic ethenate.		Diethylic ethenate.

These substitutions may be effected in various ways. The simplest is to replace an atom of hydrogen in the alcohol by potassium or sodium, and act on the resulting compound with a haloïd ether; thus:

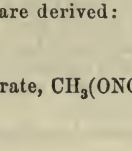
$2C_2H_4(OH)_2$	+	Na_2	=	$2C_2H_4(OH)(ONa)$	+	H_2,
Ethene alcohol.				Sodium ethenate.		

$C_2H_4(OH)(ONa)$	+	C_2H_5I	=	NaI	+	$C_2H_4(OH)(OC_2H_5)$
Sodium ethenate.		Ethyl iodide.		Sodium iodide.		Monethylic ethenate.

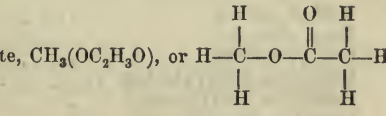
In the polyatomic alcohols, two equivalents of hydroxyl may also be replaced by one atom of oxygen, giving rise to another class of oxygen ethers; thus, from ethene alcohol, $C_2H_4(OH)_2$, is derived *ethene-oxide*, C_2H_4O.

The replacement of the hydrogen of the hydroxyl in an alcohol by acid radicals (p. 469), produces *ethereal salts* or *compound ethers:* thus from methyl alcohol, $CH_3(OH)$, are derived:

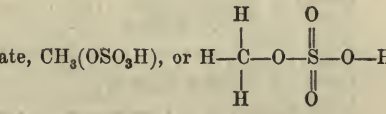
Methyl nitrate, $CH_3(ONO_2)$, or



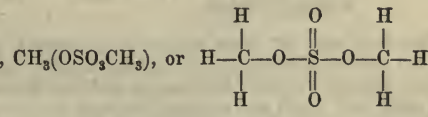
Methyl acetate, $CH_3(OC_2H_3O)$, or



Acid methyl sulphate, $CH_3(OSO_3H)$, or



Neutral methyl sulphate, $CH_3(OSO_3CH_3)$, or



It is clear that these ethereal salts may be derived from the corresponding acids by substitution of alcohol-radicals for hydrogen, being in fact related to the alcohols in the same manner as metallic salts to metallic hydrates (p. 469). When distilled with alkalies, they are resolved into an acid and alcohol; *e. g.:*

$$\underset{\text{Ethyl acetate.}}{C_2H_5(OC_2H_3O)} + \underset{\text{Potassium hydrate.}}{K(OH)} = \underset{\text{Potassium acetate.}}{K(OC_2H_3O)} + \underset{\text{Ethyl alcohol.}}{C_2H_5(OH)}$$

The action of haloïd ethers, or of certain ethereal salts, on the sulph-hydrates and sulphides of the alkali-metals, gives rise to *alcoholic sulph-hydrates* and *sulphides*, that is to say, alcohols and ethers containing sulphur in place of oxygen; thus:

$$\underset{\text{Ethyl chloride.}}{C_2H_5Cl} + KSH = KCl + \underset{\text{Ethyl sulph-hydrate.}}{C_2H_5SH}$$

$$\underset{\text{Potassium ethyl sulphate.}}{2C_2H_5OSO_3K} + \underset{\text{Potassium sulphide.}}{KSK} = \underset{\text{Potassium sulphate.}}{2KOSO_3K} + \underset{\text{Ethyl sulphide.}}{C_2H_5SC_2H_5}$$

The alcoholic sulph-hydrates, or sulphur-alcohols, are also called *mercaptans*, from their property of readily combining with mercury (*corpora mercurio apta*). Their reactions are closely analogous to those of the oxygen-alcohols.

MONATOMIC ALCOHOLS AND ETHERS.

I. Containing the radicals C_nH_{2n+1}, homologous with Methyl.

The alcohols of this series are the best known and most important of all this class of bodies. They may be formed from the corresponding haloïd ethers by the action of alkalies, and several of them are produced by the fermentation of sugar. There are also synthetical processes by which these alcohols may be built up in regular order, from the lowest upwards; but these will be better understood further on.

The names and formulæ of the known alcohols of this series are as follows:

Methyl alcohol	CH_4O
Ethyl alcohol	C_2H_6O
Propyl alcohol	C_3H_8O
Quartyl or Butyl alcohol	$C_4H_{10}O$
Quintyl or Amyl alcohol	$C_5H_{12}O$
Sextyl or Hexyl alcohol	$C_6H_{14}O$
Septyl or Heptyl alcohol	$C_7H_{16}O$
Octyl alcohol	$C_8H_{18}O$
Nonyl alcohol	$C_9H_{20}O$
Sexdecyl or Cetyl alcohol	$C_{16}H_{34}O$
Ceryl alcohol	$C_{27}H_{56}O$
Melissyl alcohol	$C_{30}H_{62}O$.

The first nine of these alcohols are liquid at ordinary temperatures. Methyl and ethyl alcohols are mobile, watery liquids; the others are more or less oily, the viscidity increasing with the molecular weight; cetyl alcohol is a solid fat; ceryl and melissyl alcohols are of waxy consistence.

The formula of methyl alcohol is that of methane or marsh-gas having one atom of hydrogen replaced by hydroxyl; and the rest may be derived from it by replacement of one or more of the other hydrogen-atoms by methyl and its homologues. If we replace only one atom of hydrogen in this manner we obtain the series:

Methyl alcohol.	Ethyl alcohol.	Propyl alcohol.	Quartyl alcohol.	Quintyl alcohol.
$C\begin{cases}H\\H\\H\\OH\end{cases}$	$C\begin{cases}CH_3\\H\\H\\OH\end{cases}$	$C\begin{cases}CH_2CH_3\\H\\H\\OH\end{cases}$	$C\begin{cases}CH_2CH_2CH_3\\H\\H\\OH\end{cases}$	$C\begin{cases}CH_2CH_2CH_2CH_3\\H\\H\\OH\end{cases}$

or:

$C\begin{cases}H\\H\\H\\OH\end{cases}$	$C\begin{cases}CH_3\\H\\H\\OH\end{cases}$	$C\begin{cases}C_2H_5\\H\\H\\OH\end{cases}$	$C\begin{cases}C_3H_7\\H\\H\\OH\end{cases}$	$C\begin{cases}C_4H_9\\H\\H\\OH\end{cases}$

Now, it is clear that, so long as the type of an alcohol is preserved — that is, of a hydrocarbon having at least one hydrogen-atom replaced by hydroxyl — the first two alcohols of this series do not admit of any other mode of formulation: in other words, these two bodies are not susceptible of isomeric modifications. But with regard to the higher members of the series the case is different. Thus, to obtain the formula of the three-carbon alcohol, C_3H_8O, instead of replacing one hydrogen-atom in methyl alcohol by ethyl, we may replace two hydrogen-atoms by methyl, which will give for this alcohol the formula $C\begin{cases}CH_3\\CH_3\\H\\OH\end{cases}$ instead of $C\begin{cases}CH_2CH_3\\H\\H\\OH\end{cases}$; and in like manner for the four-carbon alcohol, $C_4H_{10}O$, we obtain the three modifications:

Primary.	Secondary.	Tertiary.
$C\begin{cases}CH_2CH_2CH_3\\H\\H\\OH\end{cases}$	$C\begin{cases}CH_2CH_3\\CH_3\\H\\OH\end{cases}$	$C\begin{cases}CH_3\\CH_3\\CH_3\\OH\end{cases}$

An alcohol is said to be primary, secondary, or tertiary, according as the carbon-atom which is in combination with hydroxyl, is likewise directly combined with one, two, or three other carbon-atoms.

The five-carbon alcohol, and those above it, are likewise susceptible of the same three modifications, and no more, inasmuch as the carbon-atom combined with hydroxyl has only three other units of equivalency to dispose of.

There is still, however, another kind of modification of which the alcohols of each of these three groups are susceptible, arising from modifications in the alcohol-radicals themselves, already noticed in connection with the paraffins (p. 478). The primary four-carbon alcohol, for example, may be represented by either of the formulæ:

$$C\begin{cases}CH_2CH_2CH_3\\H\\H\\OH\end{cases} \qquad C\begin{cases}CH(CH_3)_2\\H\\H\\OH\end{cases}$$

Each of these fulfils the essential condition of a primary alcohol; but the first contains normal propyl, $CH_2(C_2H_5)$, whereas the second contains isopropyl, $CH(CH_3)_2$; and in the higher alcohols it is easy to see that a still larger number of modifications may exist; but only a very few of them have hitherto been actually obtained. The methods of producing secondary and tertiary alcohols, and the differences of character exhibited by the several modifications, will be explained further on.

A very convenient nomenclature for these isomeric alcohols has been proposed by Kolbe. Methyl alcohol, $CH_3(OH)$, is called *carbinol;* and the primary alcohols formed from it by successive substitution of methyl, ethyl, &c., for an atom of hydrogen, are named according to the radicals which they contain; thus,

Carbinol, or Methyl alcohol	$C(OH)H_3$
Methyl carbinol, or Ethyl alcohol	$C(OH)H_2CH_3$
Ethyl carbinol, or Propyl alcohol	$C(OH)H_2C_2H_5$
Dimethyl carbinol, or Isopropyl alcohol	$C(OH)H(CH_3)_2$
Propyl carbinol, or Quartyl alcohol	$C(OH)H_2(C_3H_7)$
Isopropyl carbinol, or Isoquartyl alcohol	$C(OH)H_2CH(CH_3)_2$
Methyl-ethyl carbinol, or Secondary Quartyl alcohol	$C(OH)HCH_3C_2H_5$
Trimethyl carbinol, or Tertiary Quartyl alcohol	$C(OH)(CH_3)_3$.

METHYL ALCOHOL AND ETHERS.

Methyl Alcohol, Hydroxymethane, or **Carbinol,** CH_4O or $CH_3(OH)$. — This is the simplest member of the series. It is produced: 1. From marsh-gas, by subjecting that compound to the action of chlorine in sunshine, whereby chloromethane, or methyl chloride, CH_3Cl, is produced, and distilling this chloride with potash.

2. From wintergreen oil, which consists chiefly of acid methyl salicylate, C_7H_4O . H . CH_3, by distillation with potash, whereby potassium salicylate is formed, and methyl alcohol distils over:

$C_7H_4O_3$. H . CH_3	+	KOH	=	$C_7H_4O_3$. H . K	+	$CH_3(OH)$
Acid methyl salicylate.		Potassium hydrate.		Acid potassium salicylate.		

This reaction, which consists in the interchange of methyl and potassium, yields very pure methyl alcohol.

3. From crude wood-vinegar, the watery liquid obtained by the destructive distillation of wood: it was in this liquid that methyl alcohol was first discovered by P. Taylor, in 1812: hence it is often called *wood-spirit.* Crude wood-vinegar probably contains about $\frac{1}{100}$ part of methyl alcohol, which is separated from the great bulk of the liquid by subjecting the whole to distillation, and collecting apart the first portions which pass over. The acid solution thus obtained is neutralized with slaked lime, and the clear liquid, separated from the oil which floats on the surface, and from the sediment at the bottom of the vessel, is again distilled. A volatile liquid is thus obtained, which burns like weak spirit; this may be strengthened by rectification, and ultimately rendered pure and anhydrous by careful distillation from quicklime at the heat of a water-bath.

Pure methyl alcohol is a colorless, thin liquid, very similar in smell and taste to ethyl alcohol; crude wood-spirit, on the other hand, which contains many impurities, has an offensive odor and a nauseous, burning taste. Methyl alcohol boils at 66·6° C. (152° F.), and has a density of 0·798 at 20° C. (68° F.). Vapor-density (referred to hydrogen) = 16. Methyl alcohol when pure mixes in all proportions with water: it dissolves resins and volatile oils as freely as ethyl alcohol, and is often substituted for ethyl alcohol in various processes in the arts, for which purpose it is prepared on a large scale. It may be burnt instead of ordinary spirit in lamps: the flame is pale-colored, like that of ethyl alcohol, and deposits no soot.

Methyl alcohol dissolves caustic baryta: the solution deposits, by evaporation in a vacuum, acicular crystals, containing $BaO.2CH_4O$. It dissolves calcium chloride in large quantity, and gives rise to a crystalline compound containing, according to Kane, $CaCl_2.2CH_4O$.

Potassium and *sodium* dissolve in it, with evolution of hydrogen yielding potassium and sodium methylates or methyl ethers, CH_3OK, and CH_3ONa.

By *oxidation*, as by exposure to the air in contact with platinum black, it is converted into formic acid, CH_2O_2, or CHO.OH, which is derived from it by substitution of 1 atom of oxygen for 2 atoms of hydrogen:

$$CH_4O + O_2 = OH_2 + CH_2O_2.$$

Methyl Chloride, or **Chloromethane**, CH_3Cl, is formed, according to Berthelot, when a mixture of equal volumes of methane (marsh-gas) and chlorine is exposed to reflected sunlight. It is more easily prepared, however, by heating a mixture of 2 parts of common salt, 1 part of wood-spirit, and 3 parts of concentrated sulphuric acid. It is a gaseous body, which may be conveniently collected over water, as it is but slightly soluble in that liquid. It is colorless; has a peculiar odor and sweetish taste, and burns, when kindled, with a pale flame, greenish towards the edges, like most combustible chlorine-compounds. Its density, referred to hydrogen as unity, is 25·25; it is not liquefied at —18° C. (0° F.). The gas is decomposed by transmission through a red-hot tube, with slight deposition of carbon, into hydrochloric acid gas and a hydrocarbon which has been but little examined. By the action of chlorine in sunshine it is successively converted into *methene chloride*, or *dichloromethane*, CH_2Cl_2, a liquid boiling at 30·5° C. (87° F.); *methenyl chloride*, *trichloromethane*, or *chloroform*, $CHCl_3$; and *carbon tetrachloride*, CCl_4.

Methyl Iodide, or **Iodomethane**, CH_3I, is a colorless and feebly combustible liquid, obtained by distilling together 1 part of phosphorus, 8 of iodine, and 12 or 15 of wood-spirit. It is insoluble in water, has a density of 2·237, and boils at 40° C. (111° F.). The density of its vapor, referred to hydrogen as unity, is 71. When digested in sealed tubes with *zinc*, it yields a colorless gaseous mixture containing ethane, or dimethyl, C_2H_6, and the residue contains zinc iodide, together with *zinc methide*, $Zn(CH_3)_2$, a very volatile liquid, which takes fire spontaneously in contact with the air:

$$2CH_3I + Zn = ZnI_2 + C_2H_6$$
$$2CH_3I + Zn_2 = ZnI_2 + Zn(CH_3)_2.$$

Methyl Ether, **Methyl Oxide**, or **Methoxyl-methane**, $C_2H_6O = (CH_3)_2O = C\begin{cases} H \\ H \\ H \\ OCH_3 \end{cases}$. — This compound, which bears the same relation to methyl alcohol that anhydrous potassium oxide bears to potassium hydrate, is produced by abstraction of the elements of water from methyl alcohol: $2CH_4O - OH_2 = C_2H_6O$.

To prepare it, 1 part of wood-spirit and 4 parts of concentrated sulphuric acid are mixed and exposed to heat in a flask fitted with a perforated cork and bent tube: the liquid slowly blackens, and emits large quantities of gas, which may be passed through a little strong solution of caustic potash, and collected over mercury. This is *methyl ether*, a permanently gaseous substance, which does not liquefy at —16° C. (3° F.). It is colorless, has an ethereal odor, and burns with a pale and feebly luminous flame. Its specific gravity is 1·617 referred to air, or 23 referred to hydrogen as unity. Cold water dissolves about 33 times its volume of this gas, acquiring thereby its characteristic taste and odor: on boiling the solution, the gas

is again liberated. Alcohol, wood-spirit, and concentrated sulphuric acid dissolve it in still larger quantity.

Methyl Nitrate, $CH_3.NO_3$, or $CH_3.ONO_2$, or $H_3C—O—\overset{\overset{O}{\|}}{N}—\underset{\underset{O}{\|}}{}$.—This ether is obtained by distilling 50 grams of pounded nitre with 50 grams of wood-spirit and 100 grams of sulphuric acid, in a retort without external heating. It is a colorless liquid of sp. gr. 1·182 at 20° C. (68° F.); boils at 66° C. (151° F.); has a faint ethereal odor. Its vapor detonates violently when heated to 150° C. (302° F.). Heated with *alcoholic ammonia*, it yields methylamine nitrate, $CH_5N.NO_3H$. Distilled with aqueous *potash*, it yields methyl ether.

Methyl Sulphates,—Sulphuric acid being a bibasic acid, yields two methyl ethers—one acid, the other neutral.

Acid methylsulphate, *Methyl* and *Hydrogen sulphate*, *Methylsulphuric acid*, or *Sulphomethylic acid*, $CH_3.H.SO_4$, or $CH_3.OSO_3H=H_3C—O—\overset{\overset{O}{\|}}{S}—OH$.—To prepare this acid ether, 1 part of wood-spirit is slowly mixed with 2 parts of concentrated sulphuric acid, and the whole is heated to ebullition, and left to cool, after which it is diluted with water, and neutralized with barium carbonate. The solution is filtered from the insoluble sulphate, and evaporated, first in a water-bath, and afterwards in a vacuum to the proper degree of concentration. The salt crystallizes in beautiful, square, colorless tables, containing $(CH_3)_2Ba''SO_4.2OH_2$, which effloresce in dry air, and are very soluble in water. By exactly precipitating the base from this substance with dilute sulphuric acid, and leaving the filtered liquid to evaporate in the air, methylsulphuric acid may be procured in the form of a sour, syrupy liquid, or in minute acicular crystals, very soluble in water and alcohol. It is very instable, being easily decomposed by heat. *Potassium methylsulphate*, CH_3KSO_4, crystallizes in small, nacreous, deliquescent rhombic tables. The *lead-salt* is also very soluble.

Neutral Methyl sulphate, or *Dimethylic sulphate*, $(CH_3)_2SO_4$, or $CH_3.OSO_3CH_3$, or $H_3C—O—\overset{\overset{O}{\|}}{S}—O—CH_3$.—This ether is prepared by distilling 1 part of wood-spirit with 8 or 10 parts of strong oil of vitriol; the distillation may be carried nearly to dryness. The oleaginous liquid found in the receiver is agitated with water, and purified by rectification from powdered caustic baryta. The product is a colorless, oily liquid, of alliaceous odor, having a density of 1·324, and boiling at 188° C. (370° F.). It is neutral to test paper, and insoluble in water, but decomposed by that liquid, slowly in the cold, rapidly and with violence at a boiling temperature, into methylsulphuric acid and wood-spirit. Anhydrous lime and baryta have no action on this ether: their hydrates, however, and those of potassium and sodium, decompose it instantly, with production of a methylsulphate of the base, and methyl alcohol. When neutral methylsulphate is heated with common salt, it yields sodium sulphate and methyl chloride; with mercuric cyanide, or potassium cyanide, it gives a sulphate

of the base, and methyl cyanide; with dry sodium formate, it yields sodium sulphate and methyl formate

Methyl Borate, $(CH_3)_3BO_3 = B'''(OCH_3)_3$, is formed by the action of gaseous boron chloride on anhydrous methyl alcohol. It is a limpid liquid, of specific gravity 0·9551 at 0°, boiling at 72° C. (162° F.). Water decomposes it into boric acid and methyl alcohol.

Methyl Phosphates.—Two methyl phosphates have been obtained, viz., methylphosphoric acid, $(PO)'''(OH)_2(OCH_3)$, and dimethylphosphoric acid, $(PO)'''(OH)(OCH_3)_2$. They are formed by the action of phosphorus oxychloride on methyl alcohol under different circumstances.

Methyl Silicate, $Si^{iv}(OCH_3)_4$, is obtained by acting upon perfectly pure and dry methyl alcohol with silicium tetrachloride, and distilling the product. It is a colorless liquid, of pleasant, ethereal odor, specific gravity 1·0589 at 0°, distilling between 121° and 126° C. (250°–258° F.). It dissolves with moderate facility in water, and the solution does not become turbid from separation of silica for some weeks. Its observed vapor-density is 5·38 referred to air, or 312 referred to hydrogen, the calculated number being 304.

Hexmethyl-disilicic ether, $(CH_3)_6Si_2O_7$, or $Si^{iv}_2O(OCH_3)_6$, is produced, together with the compound last described, when the methyl alcohol used is not quite dry. It boils at 201° to 202·5° C. (294°–295° F.), and has a density of 1·1441 at 0°. In other respects it resembles the preceding.

Methyl Sulph-hydrate, CH_3SH, also called **Methyl Mercaptan.**—This compound, which has the composition of methyl alcohol with the oxygen replaced by sulphur, is formed by distilling in a water-bath, with efficient condensation, a mixture of calcium methylsulphate and potassium sulphhydrate:

$$(SO_4)_2(CH_3)_2Ca'' + 2KSH = SO_4K_2 + SO_4Ca + 2CH_3SH.$$

It is a liquid lighter than water, and having an extremely offensive odor. It forms with lead-acetate a yellow precipitate, and with mercuric oxide a white compound, $(CH_3)_2S_2Hg''$, which crystallizes from alcohol in shining laminæ.

Methyl Sulphide, $S(CH_3)_2$, or H_3CSCH_3, is obtained by passing gaseous methyl chloride into a solution of potassium monosulphide in wood-spirit. It is a colorless, mobile, fetid liquid, of specific gravity 0·845 at 21° C. (76° F.), boiling at 41° C. (106° F.). It forms several substitution-products with chlorine.

Methyl Bisulphide, $(CH_3)_2S_2$, is prepared by passing gaseous methyl chloride through an alcoholic solution of potassium bisulphide. It is a limpid, strongly refracting liquid, having a specific gravity of 1·046 at 18°, and an intolerable odor of onions; boils between 116° and 118°. It forms substitution-products with bromine and chlorine.

By substituting pentasulphide for bisulphide of potassium in the preceding preparation, a *trisulphide of methyl,* $(CH_3)_2S_3$, is obtained, boiling at about 200°.

ETHYL ALCOHOL AND ETHERS.

Ethyl Alcohol, Hydroxyl-ethane, or **Methyl Carbinol,**

$$C_2H_6O = C_2H_5(OH) = \begin{matrix} CH_3 \\ | \\ CH_2(OH) \end{matrix} = C\begin{Bmatrix} CH_3 \\ H \\ H \\ OH \end{Bmatrix}$$

This important compound, the oldest and best known of the whole group of alcohols, and generally designated by the simple name "alcohol," is produced:

1. From ethene, C_2H_4, by addition of the elements of water. When ethene gas and strong sulphuric acid are violently agitated together for a long time, the gas is absorbed, and ethylsulphuric acid, $C_2H_6SO_4$, is produced; and this compound, distilled with water, yields sulphuric acid and ethyl alcohol:

$$C_2H_6SO_4 + OH_2 = SO_4H_2 + C_2H_6O.$$

Now we have seen that ethene can be formed by addition of hydrogen to ethine, C_2H_2, which is itself formed by direct combination of carbon and hydrogen. It follows, therefore, that alcohol can be produced synthetically from its elements.

2. By the fermentation of certain kinds of sugar. When a moderately warm solution of cane-sugar or grape-sugar (glucose) is mixed with certain albuminous matters, as blood, white of egg, flour-paste, and especially beer-yeast, in a state of decomposition, a peculiar process, called *fermentation*, is set up, by which the sugar is resolved into ethyl alcohol and carbon dioxide. In the case of glucose, these products result from a simple splitting up of the molecule:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2} + \underset{\text{Alcohol.}}{2C_2H_6O.}$$

Cane sugar, $C_{12}H_{12}O_{11}$, is first converted into glucose by assumption of water ($C_{12}H_{22}O_{11} + OH_2 = 2C_6H_{12}O_6$), and the latter is then decomposed as above.*

If ordinary cane-sugar be dissolved in a large quantity of water, a due proportion of active yeast added, and the whole maintained at a temperature of 21°–26° C. (70°–80° F.), the change will go on with great rapidity. The gas disengaged is nearly pure carbon dioxide: it is easily collected and examined, as the fermentation, once commenced, proceeds perfectly well in a close vessel, such as a large bottle or flask fitted with a cork and a conducting-tube. When the effervescence is at an end, and the liquid has become clear, it will yield alcohol by distillation.

The spirit first obtained by distilling a fermented saccharine liquid is very weak, being diluted with a large quantity of water. By a second distillation, in which the first portions of the distilled liquid are collected apart, it may be greatly strengthened: the whole of the water cannot, however, be thus removed. The strongest rectified spirit of wine of commerce has a density of about 0·835, and yet contains 13 or 14 per cent. of water. Pure or *absolute* alcohol may be obtained from it by redistilling it with half its weight of fresh quicklime. The lime is reduced to coarse powder, and put into a retort; the alcohol is added, and the whole mixed by agitation. The neck of the retort is securely stopped with a cork and the mixture left for several days. The alcohol is distilled off by the heat of a water-bath.

Pure alcohol is a colorless, limpid liquid, of pungent and agreeable taste and odor; its specific gravity, at 15·5° C. (60° F.), is 0·7938, and that of its vapor referred to air, 1·613. It is very inflammable, burning with a pale-bluish flame, free from smoke; it has never been frozen. Alcohol boils at 78·4° C. (173° F.) when in the anhydrous state; in a diluted state the boil-

* Side by side with this principal decomposition, a variety of other changes are simultaneously accomplished. According to Pasteur, glycerine, succinic acid, cellulose, fats, and occasionally lactic acid, are observed among the products of alcoholic fermentation. Some of the homologues of ethyl alcohol are also found among the products.

ing point is higher, being progressively raised by each addition of water. In the act of dilution a contraction of volume occurs, and the temperature of the mixture rises many degrees: this takes place not only with pure alcohol, but also with rectified spirit. Alcohol is miscible with water in all proportions, and, indeed, has a great attraction for the latter, absorbing its vapor from the air, and abstracting the moisture from membranes and other similar substances immersed in it. The solvent powers of alcohol are very extensive: it dissolves a great number of saline compounds, and likewise a considerable proportion of potash. With some salts it forms definite crystalline compounds, called *alcoholates:* with *zinc chloride*, $ZnCl_2 . 2C_2H_6O$; with *calcium chloride*, $CaCl_2 . 4C_2H_6O$; with *magnesium nitrate*, $(NO_3)_2Mg . 6C_2H_6O$. Alcohol dissolves, moreover, many organic substances, as the vegeto-alkalies, resins, essential oils, and various other bodies: hence its great use in chemical investigations and in several of the arts.

Potassium and *sodium* dissolve in ethyl alcohol in the same manner as in methyl alcohol, forming the compounds C_2H_5KO and C_2H_5NaO.

Alcohol, passed through a red-hot tube, is resolved into marsh-gas, hydrogen, and carbon monoxide:

$$C_2H_6O = CH_4 + H_2 + CO.$$

Small quantities of ethene, benzene, and naphthalene are, however, formed at the same time by the mutual action of these primary products, and carbon is deposited.

By *oxidation*, alcohol is converted, first, into aldehyde, then into acetic acid:

$$\underset{\text{Alcohol.}}{C_2H_6O} + O = OH_2 + \underset{\text{Aldehyde.}}{C_2H_4O},$$

$$\underset{\text{Aldehyde.}}{C_2H_4O} + O = \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

Chlorine gas is rapidly absorbed by anhydrous alcohol, imparting to it a yellow color, and causing considerable rise of temperature. At the same time it rapidly abstracts hydrogen, which is partly replaced by the chlorine, producing hydrochloric acid, aldehyde, acetic acid, ethyl acetate, ethyl chloride, and finally chloral. The mixture of these substances, freed by water from the soluble constituents, was formerly called *heavy muriatic ether*. The formation of the several products is represented by the following equations:

$$\underset{\text{Alcohol.}}{C_2H_6O} + Cl_2 = 2HCl + \underset{\text{Aldehyde.}}{C_2H_4O},$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + 4Cl_2 = 5HCl + \underset{\text{Chloral.}}{C_2HCl_3O},$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + HCl = OH_2 + \underset{\text{Ethyl chloride.}}{C_2H_5Cl},$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + OH_2 + 2Cl_2 = 4HCl + \underset{\text{Acetic acid.}}{C_2H_4O_2},$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Acetic acid.}}{C_2H_4O_2} = OH_2 + \underset{\text{Ethyl acetate.}}{C_2H_3O_2.C_2H_5}.$$

When the action of the chlorine is continued for a long time, *chloral* is always the principal product. This compound is a heavy oily liquid, having the composition of aldehyde with 3 atoms of hydrogen replaced by chlorine;

but it cannot be formed by the direct action of chlorine upon aldehyde. When alcohol containing water is used, scarcely any chloral is obtained, the chief product being aldehyde.

Chlorine, in presence of *alkalies*, converts alcohol into chloroform and carbon dioxide:

$$\underset{\text{Alcohol.}}{C_2H_6O} + 4Cl_2 + OH_2 = CO_2 + 5HCl + \underset{\text{Chloroform.}}{CHCl_3}.$$

The same products are formed by distilling dilute alcohol with bleaching powder.

Aqueous alcohol heated with strong *sulphuric acid* is converted into ethylsulphuric acid, $C_2H_6SO_4$, or $C_2H_5(OSO_3H)$, (p. 526); but when anhydrous alcohol is exposed to the vapor of sulphuric oxide, SO_3, a white crystalline substance is formed, called *ethionic oxide*, formerly *sulphate* of *carbyl*, $C_2H_4S_2O_6$. This, when dissolved in water or in aqueous alcohol, is converted into *ethionic acid*, $C_2H_6S_2O_7$, a bibasic acid, which forms a soluble barium salt. Lastly, a solution of ethionic acid, when boiled, is resolved into sulphuric acid and *isethionic acid*, an acid isomeric with ethylsulphuric acid (p. 527).

Commercial Spirit, Wine, Beer, &c. Vinous Fermentation.—The strength of commercial spirit, when free from sugar and other substances added subsequent to distillation, is inferred from its density: a table exhibiting the proportions of real alcohol and water in spirits of different densities will be found at the end of the volume. The excise *proof spirit* has a sp. gr. of 0·9198 at 60° F., and contains 49½ per cent. by weight of real alcohol.

The high duty on spirits of wine in this country has hitherto interfered with the development of many branches of industry, which are dependent on the free use of this important liquid. The labors of the scientific chemist have been likewise often checked by this inconvenience. A remedy for the evil has been supplied in Great Britain by a very important measure, proposed and carried out by the late Mr. John Wood, Chairman of the Board of Inland Revenue. This measure consists in issuing for manufacturing and scientific purposes, duty free, a mixture of 90 per cent. of spirits of wine of not less strength than corresponds to a density of 0·830, with 10 per cent. of partially purified wood-spirit, which is now sold by licensed dealers under the name of *Methylated Spirit*. It appears that a mixture of this kind is rendered permanently unfit for human consumption, the separation of the two substances, in consequence of their close analogy, being not only difficult, but to all appearance impossible: at the same time, and for the same reasons, this mixture is not materially impaired for the greater number of the more valuable purposes in the arts to which spirits are usually employed. Methylated spirit may be used, instead of pure spirit, as a solvent of resinous substances, and of many chemical preparations, especially of the alkaloïds and other organic products. It may be used for the production of fulminating mercury, ether, chloroform, iodoform, olefiant gas, and all its derivatives — in fact, for an endless number of laboratory purposes. Mythylated spirit may also be substituted for pure spirit of wine in the preservation of anatomical preparations. The introduction of this spirit has already exerted a very beneficial effect upon the development of organic chemistry in that country.*

* See Report on the Supply of Spirits of Wine, free from duty, for use in the Arts and Manufactures, addressed to the Chairman of Inland Revenue, by Professors Graham, Hofmann, and Redwood. (Quarterly Journal of Chemical Society, vol. viii. p. 120.

Wine, beer, &c., owe their intoxicating properties to the alcohol they contain, the quantity of which varies very much. Port and sherry, and some other strong wines, contain, according to Mr. Brande, from 19 to 25 per cent. of alcohol, while in the lighter wines of France and Germany it sometimes falls as low as 12 per cent. Strong ale contains about 10 per cent.; ordinary spirits, as brandy, gin, whiskey, 40 to 50 per cent., or occasionally more. These latter owe their characteristic flavors to certain essential oils, present in very small quantity, either generated in the act of fermentation or purposely added.

In making wine, the expressed juice of the grape is simply set aside in large vats, where it undergoes spontaneously the necessary change. The vegetable albumin of the juice absorbs oxygen from the air, runs into decomposition, and in that state becomes a ferment to the sugar, which is gradually converted into alcohol. If the sugar be in excess, and the azotized matter deficient, the resulting wine remains sweet; but if, on the other hand, the proportion of sugar be small and that of albumen large, a *dry* wine is produced. When the fermentation stops, and the liquor becomes clear, it is drawn off from the lees, and transferred to casks, to ripen and improve.

The color of red wine is derived from the skins of the grapes, which in such cases are left in the fermenting liquid. Effervescent wines, as champagne, are bottled before the fermentation is complete; the carbonic acid is disengaged under pressure, and retained in solution in the liquid. A certain quantity of sugar is frequently added. The process requires much delicate management.

During the fermentation of the grape-juice, or *must*, a crystalline, stony matter, called *argol*, is deposited. This consists chiefly of acid potassium tartrate with a little coloring matter, and is the source of all the tartaric acid met with in commerce. The salt in question exists in the juice in considerable quantity; it is but sparingly soluble in water, but still less so in dilute alcohol: hence, as the fermentation proceeds, and the quantity of spirit increases, it is slowly deposited. The acid of the juice is thus removed as the sugar disappears. It is this circumstance which renders grape-juice alone fit for making good wine; when that of gooseberries or currants is employed as a substitute, the malic and citric acids which these fruits contain cannot be thus withdrawn. There is then no other resource but to add sugar in sufficient quantity to mask and conceal the natural acidity of the liquor. Such wines are necessarily acescent, prone to a second fermentation, and, to many persons, at least, very unwholesome.

Beer is a well-known liquor, of great antiquity, prepared from germinated grain, generally barley, and is used in countries where the wine does not flourish. The operation of *malting* is performed by steeping the barley in water until the grains become swollen and soft, then piling it in a heap or *couch*, to favor the elevation of temperature caused by the absorption of oxygen from the air, and afterwards spreading it upon a floor, and turning it over from time to time to prevent unequal heating. When germination has proceeded far enough, the vitality of the seed is destroyed by kiln-drying. During this process, a peculiar nitrogenous substance called *diastase* is produced, which acts as a ferment on the starch of the grain, converting a portion of it into sugar and rendering it soluble.

In brewing, the crushed malt is infused in water at about 77° C. (170° F.), and the mixture is left to stand during the space of two hours or more. The easily soluble diastase has thus an opportunity of acting upon the unaltered starch of the grain, and changing it into dextrin and sugar. The clear liquor, or *wort*, strained from the exhausted malt, is next pumped up into a copper boiler, and boiled with the requisite quantity of hops, to communicate a pleasant bitter flavor, and confer on the beer the property of

keeping without injury. The flowers of the hop contain a bitter, resinous principle, called *lupulin*, and an essential oil.

When the wort has been sufficiently boiled, it is drawn from the copper, and cooled as rapidly as possible, to near the ordinary temperature of the air, in order to avoid an irregular acid fermentation, to which it would otherwise be liable. It is then transferred to the fermenting vessels, which in large breweries are of great capacity, and mixed with a quantity of yeast, the product of a preceding operation, by which the change is speedily induced. This is the most critical part of the whole operation, and one in which the skill and judgment of the brewer are most called into play. The process is in some measure under control by attention to the temperature of the liquid; and the extent to which the change has been carried is easily known by the diminished density, or *attenuation* of the wort. The fermentation is never suffered to run its full course, but is always stopped at a particular point, by separating the yeast, and drawing off the beer into casks. A slow and almost insensible fermentation succeeds, which in time renders the beer stronger and less sweet than when new, and charges it with carbonic acid.

Highly colored beer is made by adding to the malt a small quantity of strongly dried or charred malt, the sugar of which has been changed to caramel; porter and stout are so prepared.

The yeast of beer is a very remarkable substance, and has excited much attention. To the naked eye it is a greenish-yellow soft solid, nearly insoluble in water, and dries up to a pale-brownish mass, which readily putrefies when moistened, and becomes offensive. Under the microscope it exhibits a kind of organized appearance, being made up of little transparent globules, which sometimes cohere in clusters or strings, like some of the lowest members of the vegetable kingdom. Whatever may be the real nature of the substance, no doubt can exist that it is formed from the soluble azotized portion of the grain during the fermentative process. No yeast is ever produced in liquids free from azotized matter; that added for the purpose of exciting fermentation in pure sugar is destroyed, and rendered inert thereby. When yeast is deprived, by straining and strong pressure, of as much water as possible, it may be kept in a cool place, with unaltered properties, for a long time; otherwise it speedily spoils.

The distiller, who prepares spirits from grain, makes his wort, or *wash*, much in the same manner as the brewer; he uses, however, with the malt a large quantity of raw grain, the starch of which suffers conversion into sugar by the diastase of the malt, which is sufficient for his purpose. He does not boil his infusion with hops, but proceeds at once to the fermentation, which he pushes as far as possible by large and repeated doses of yeast. Alcohol is manufactured in many cases from potatoes. The potatoes are ground to pulp, mixed with hot water and a little malt, to furnish diastase, made to ferment, and then the fluid portion is distilled. The potato-spirit is contaminated by a very offensive volatile oil, again to be mentioned: the crude product from corn contains a substance of a similar kind. The business of the rectifier consists in removing or modifying these volatile oils, and in replacing them by others of a more agreeable character.

In making *bread*, the vinous fermentation plays an important part: the yeast added to the dough converts the small portion of sugar the meal naturally contains into alcohol and carbonic acid. The gas thus disengaged forces the tough and adhesive materials into bubbles, which are still further expanded by the heat of the oven, which at the same time dissipates the alcohol: hence the light and spongy texture of all good bread. The use of *leaven* is of great antiquity: this is merely dough in a state of incipient putrefaction. When mixed with a large quantity of fresh dough, it excites in the latter the alcoholic fermentation, in the same manner as yeast, but

less perfectly; it is apt to communicate a disagreeable sour taste and odor. Sometimes carbonate of ammonia is employed to lighten the dough, being completely volatilized by the high temperature of the oven. Bread is now sometimes made by mixing a little hydrochloric acid and sodium carbonate in the dough; if proper proportions be taken and the whole thoroughly mixed, the operation appears to be very successful.

Another mode of bread-making, now practised on a large scale with great success, is that invented by the late Dr. Dauglish, which consists in agitating the dough in a strong vessel with water saturated under pressure with carbonic acid gas. When the dough thus treated is subsequently released from this pressure and exposed to the air, the gas escapes in bubbles, and lightens the mass as effectually as that evolved within its substance by fermentation. The bread thus made, called "aërated bread," is of excellent quality, not being subject to the deterioration which so frequently takes place in ordinary bread, when the fermentation is allowed to go too far.

Vinous fermentation, that is to say the conversion of sugar into alcohol and carbon dioxide, never takes place except in presence of some nitrogenous body of the albuminoid class in a state of decomposition (p. 463). The manner in which these bodies act in inducing fermentation is very obscure: they neither add anything to the sugar nor take anything from it; but the motion or disturbance of their particles, while undergoing putrefaction, is supposed to be communicated to the particles of the sugar with which they are in contact, and thus to induce the decomposition above mentioned; hence such bodies are called *ferments*. There are other modes of fermentation, which sugar and substances allied to it are capable of undergoing, and the particular change induced varies with the kind of ferment present: thus vinous fermentation is induced with peculiar facility by yeast; lactous fermentation, or the conversion of sugar into lactic acid, by putrefying cheese. Another very remarkable circumstance connected with fermentation is that it is always accompanied by the development of certain minute living organisms—fungi and infusoria—like those already mentioned as existing in yeast. So constantly indeed is this the case, that many chemists and physiologists regard these organisms as the exciting cause of fermentation and putrefaction; and this view appears to be corroborated by the fact that each particular kind of fermentation takes place most readily in contact with a certain living organism, or at least with nitrogenous matter containing it; thus beer-yeast contains two species of fungus, called *Torvula cerevisiæ* and *Penicillium glaucum*, the cells of which are of very different sizes, so that they may be separated by filtering an infusion of the yeast, the larger cells of the *Torvula* remaining on the filter, while those of the *Penicillium*, which are much smaller, pass through with the liquid. Now, it is found that the residue on the filter brings a solution of sugar into the state of vinous fermentation, whereas the filtered liquid induces lactous fermentation. But whether this effect is due to the fungi themselves, or to the peculiar state of the albuminous matter in which they occur, is a question not yet decided. The investigation is attended with peculiar difficulties, arising chiefly from the universal diffusion of the germs of these minute organisms, which are present not only in all decaying albuminous matter, and on the skins of fruits, leaves, and other parts of plants, but are likewise diffused through the air; so that in experiments made for the purpose of ascertaining whether fermentation can take place without them, it is extremely difficult to insure their complete exclusion from the substances under examination.*

* See the article "Fermentation," in Watts's Dictionary of Chemistry, vol. ii. p. 623.

ETHYLIC ETHERS.

Ethyl Chloride, or Chlorethane, C_2H_5Cl, or $C\begin{cases}CH_3\\H_2\\Cl\end{cases}$, often called *Hydrochloric ether.*—To prepare this compound, rectified spirit of wine is saturated with dry hydrochloric acid gas, and the product distilled with very gentle heat; or a mixture of 3 parts oil of vitriol and 2 parts of alcohol is poured upon 4 parts of dry common salt in a retort, and heat applied; in either case the vapor of the hydrochloric ether should be conducted through a little tepid water in a wash-bottle, and then conveyed into a small receiver surrounded by ice and salt. It is purified from adhering water by contact with a few fragments of fused calcium chloride. Hydrochloric ether is a thin, colorless, and excessively volatile liquid, of a penetrating, aromatic, and somewhat alliaceous odor. At the freezing point of water, its sp. gr. is 0·921, and it boils at 12·5° C. (55° F.); it is soluble in 10 parts of water, is but incompletely decomposed by solution of silver nitrate when the two are heated together in a sealed tube, but is quickly resolved into potassium chloride and ethyl alcohol by a hot aqueous solution of caustic potash:

$$C_2H_5Cl + KOH = KCl + C_2H_5OH.$$

With alcoholic potash, on the other hand, or potassium ethylate, it yields ethyl-oxide, or common ether:

$$C_2H_5Cl + C_2H_5OK = KCl + (C_2H_5)_2O.$$

Heated with soda-lime, it yields ethene or olefiant gas:

$$2C_2H_5Cl + ONa_2 = 2NaCl + OH_2 + C_2H_4.$$

When vapor of ethyl chloride is mixed with chlorine gas in a vessel exposed first to diffused daylight, and afterwards to direct sunshine, hydrochloric acid is formed, and the chlorine displaces one atom of hydrogen in the ethyl chloride, producing monochlorinated ethyl chloride, or dichlorethane, $C_2H_4Cl_2$, a colorless, oily liquid, isomeric with ethene chloride or Dutch liquid. By the prolonged action of chlorine in excess, the compounds $C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2HCl_5, and C_2Cl_6 are produced, the last of which is a crystalline body, identical with the carbon trichloride produced by the action of chlorine on Dutch liquid.

Ethyl Bromide, or Bromethane, C_2H_5Br, also called *Hydrobromic ether*, is prepared by distilling a mixture of 8 parts bromine, 1 part phosphorus, and 39 parts alcohol. It is a very volatile liquid, heavier than water, having a penetrating taste, and odor, boiling at 41° C. (106° F.).

Ethyl Iodide, or Iodethane, C_2H_5I, also called *Hydriodic ether*, may be conveniently prepared with 5 parts of phosphorus, 70 parts of alcohol (of 0·84 sp. gr.) and 100 parts of iodine. The phosphorus is introduced into a tubulated retort, covered with part of the alcohol, and heated to fusion. The rest of the alcohol is poured upon the iodine, and the solution thus obtained is allowed to flow gradually through a tap-funnel into the retort. The brown liquid is at once decolorized, and ethyl iodide distils over, which is condensed by a good cooling apparatus. The distillate, consisting of alcohol and ethyl iodide, is again poured on the residuary iodine, which is thus rapidly dissolved, introduced into the retort, and ultimately entirely converted into ethyl iodide. The latter is washed with water to remove adhering alcohol, separated from this water by a tap-funnel, digested with calcium chloride, and rectified in the water-bath. Ethyl iodide may also be formed by heating in a sealed glass vessel a mixture of hydriodic acid and olefiant gas. Hydriodic ether is a colorless liquid, of penetrating ethe-

real odor, having a density of 1·92, and boiling at 72° C. (162° F.). It becomes red by exposure to light, from a commencement of decomposition. This substance has become highly important as a source of ethyl, and from its remarkable deportment with ammonia, which will be discussed in the Section on Organic Bases.

Ethyl Oxide, or Ethylic ether, $C_4H_{10}O=C_2H_5(OC_2H_5)=(C_2H_5)_2O$. This compound, also called *common ether*, or simply *ether*, contains the elements of 2 molecules of alcohol *minus* 1 molecule of water:

$$2C_2H_6O \quad - \quad OH_2 \quad = \quad C_4H_{10}O;$$

and it is in fact produced by the action of various dehydrating agents, such as zinc chloride, phosphoric oxide, and strong sulphuric acid, upon alcohol. The process does not appear, however, to be one of direct dehydration, at least in the case of sulphuric acid; for when that acid is heated with alcohol to a certain temperature, it does not become weaker by taking water from the alcohol, but ether and water distil over together, and the sulphuric acid remains in its original state, ready to act in the same manner on a fresh portion of alcohol. The reaction is in fact one of substitution, the ultimate result being the conversion of alcohol, $C_2H_5(OH)$, into ether, $C_2H_5(OC_2H_5)$, by the substitution of ethyl for hydrogen. The manner in which this takes place will be better understood when another mode of the formation of ether has been explained.

When a solution of sodium ethylate, C_2H_5ONa, in anhydrous alcohol, obtained by dissolving sodium to saturation in that liquid, is mixed with ethyl iodide, double decomposition takes place, resulting in the formation of sodium iodide and ethyl oxide:

$$C_2H_5ONa \; + \; C_2H_5I \; = \; NaI \; + \; C_2H_5(OC_2H_5O).$$

The result would be the same if chloride or bromide of ethyl were substituted for the iodide: moreover, when methyl iodide is added, instead of the ethyl iodide, an oxygen ether is formed containing both ethyl and methyl:

C_2H_5ONa	+	CH_3I	=	NaI	+	$C_2H_5OCH_3$.
Sodium ethylate.		Methyl iodide.				Methyl-ethyl ether.

In each case the reaction consists in an interchange between the sodium and the alcohol-radical.

Now, when alcohol is heated with strong sulphuric acid, the first result is the formation of ethylsulphuric acid, $SO_2(OC_2H_5)OH$, by substitution of ethyl for hydrogen in the acid:

$SO_2(OH)(OH)$	+	$C_2H_5(OH)$	=	$H(OH)$	+	$SO_2(OC_2H_5)(OH)$;
Sulphuric acid.		Alcohol.		Water.		Ethylsulphuric acid.

and when the ethylsulphuric acid thus formed is brought in contact, at a certain temperature, with a fresh portion of alcohol, the reverse substitution takes place, resulting in the formation of ethyl oxide and sulphuric acid:

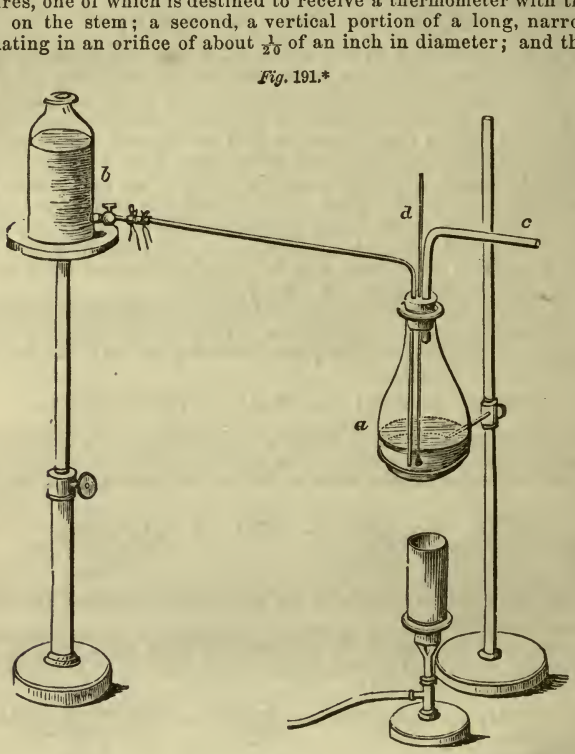
$SO_2(OC_2H_5)(OH)$	+	$C_2H_5(OH)$	=	$C_2H_5(OC_2H_5)$	+	$SO_4(OH)_2$
Ethylsulphuric acid.		Alcohol.		Ether.		Sulphuric acid.

The sulphuric acid is thus reproduced in its original state, and if the supply of alcohol be kept up, and the temperature maintained within certain limits, the same series of actions is continually repeated, and ether and water distil over together.

The most favorable temperature for etherification is between 127° and 154° C. (260° and 310° F.); below 127° very little ether is produced, and above 154° a different reaction takes place, resulting in the formation of olefiant gas. The maintenance of the temperature within the ether-producing limits is best effected by boiling the mixture of sulphuric acid and alcohol in a flask into which a further quantity of alcohol is supplied in a continuous and regulated stream. This is called the *continuous* ether process.

A wide-necked flask is fitted with a sound cork, perforated by three apertures, one of which is destined to receive a thermometer with the graduation on the stem; a second, a vertical portion of a long, narrow tube, terminating in an orifice of about $\frac{1}{20}$ of an inch in diameter; and the third,

Fig. 191.*



a wide bent tube, connected with the condenser, to carry off the volatilized products. A mixture is made of 8 parts by weight of concentrated sulphuric acid, and 5 parts of rectified spirit of wine, of about 0·834 sp. gr. This is introduced into the flask, and heated by a lamp. The liquid soon boils, and the thermometer very shortly indicates a temperature of 140° C. (284° F.). When this happens, alcohol of the above density is suffered slowly to enter by the narrow tube, which is put into communication with a reservoir of that liquid, consisting of a large bottle perforated by a hole

* Fig. 191. Apparatus for the preparation of ether. *a*. Flask for containing the mixture of oil of vitriol and alcohol. *b*. Reservoir with stopcock, for supplying a constant stream of alcohol. *c*. Wide bent tube connected with the condenser for conveying away the vapors. *d*. The thermometer for regulating the temperature of the boiling liquid.

near the bottom, and furnished with a small brass stopcock fitted by a cork. The stopcock is secured to the end of the long tube by a caoutchouc connector. As the tube passes nearly to the bottom of the flask, the alcohol gets thoroughly mixed with the acid liquid, the hydrostatic pressure of the fluid column being sufficient to insure the regularity of the flow; the quantity is easily adjusted by the aid of the stopcock. For condensation a Liebig's condenser may be used, supplied with ice-water. The arrangement is shown in figure 191.

The intensity of the heat, and the supply of alcohol, must be so adjusted that the thermometer may remain at 140° C. (284° F.), or as near that temperature as possible, while the contents of the flask are maintained in a state of *rapid and violent ebullition* — a point of essential importance. Ether and water distil over together, and collect in the receiver, forming two distinct strata: the mixture slowly blackens, from some slight secondary action of the acid upon the spirit, or upon the impurities in the latter, but retains, after many hours' ebullition, its etherifying powers unimpaired. The acid, however, slowly volatilizes, partly in the state of *oil of wine*, and the quantity of liquid in the flask is found, after the lapse of a considerable interval, sensibly diminished. The loss of acid constitutes the only limit to the duration of the process, which might otherwise be continued indefinitely.

On the large scale, the flask may be replaced by a vessel of lead, the tubes being also of the same metal: the stem of the thermometer may be made to pass air-tight through the cover, and heat may perhaps be advantageously applied by high-pressure steam, or hot oil, circulating in a spiral tube of metal immersed in the mixture of acid and spirit.

The crude ether is to be separated from the water on which it floats, agitated with a little solution of caustic potash, and re-distilled by the heat of warm water. The aqueous portion, treated with an alkaline solution, and distilled, yields alcohol containing a little ether. Sometimes the spontaneous separation before mentioned does not occur, from the accidental presence of a larger quantity than usual of undecomposed alcohol; the addition of a little water, however, always suffices to determine it.

Pure ethylic ether is a colorless, transparent, fragrant liquid, very thin and mobile. Its sp. gr. at 15·5° is about 0·720; it boils at 35·6° C. (96° F.) under the pressure of the atmosphere, and bears without freezing the severest cold. When dropped on the hand it occasions a sharp sensation of cold, from its rapid volatilization. Ether is very combustible, and burns with a white flame, generating water and carbon dioxide. Although the substance itself is one of the lightest of liquids, its vapor is very heavy, having a density of 2·586 (referred to air). Mixed with oxygen gas, and fired by the electric spark, or otherwise, it explodes with the utmost violence. Preserved in an imperfectly stopped vessel, ether absorbs oxygen, and becomes acid from the production of acetic acid: this attraction for oxygen is increased by elevation of temperature. It is decomposed by transmission through a red-hot tube into ethene, methane, aldehyde, and ethine, and two substances yet to be described.

Ether is miscible with alcohol in all proportions, but not with water; it dissolves to a small extent in that liquid, 10 parts of water taking up about 1 part of ether. It may be separated from alcohol, provided the quantity of the latter is not excessive, by addition of water, and in this manner samples of commercial ether may be conveniently examined. Ether dissolves oily and fatty substances generally, and phosphorus to a small extent, also a few saline compounds and some organic principles; but its powers in this respect are much more limited than those of alcohol or water.

Anhydrous ether, subjected to the action of chlorine, yields the three substitution-products $C_4H_8Cl_2O$, $C_4H_6Cl_4O$, and $C_4Cl_{10}O$, the first two of which are liquids, while the third, produced by the prolonged action of chlorine on ether in sunshine, is a crystalline solid. The second chlorine compound

is converted by hydrogen sulphide into the two crystalline compounds $C_4H_6Cl_2SO$ and $C_4H_6S_2O$.

Ethyl-methyl oxide, *Ethyl-methyl ether*, *Ethyl methylate*, or *Methyl ethylate*, $C_3H_8O = C_2H_5OCH_3$, is produced, as already mentioned, by the action of methyl iodide on potassium ethylate, or of ethyl iodide on potassium methylate. It is a very inflammable liquid, boiling at 11° C. (52° F.).

Ethyl Nitrate, $C_2H_5NO_3$, or $C_2H_5ONO_2$.—*Nitric ether.*—When nitric acid is heated with alcohol alone, part of the alcohol is oxidized, and the nitric acid is reduced to nitrous acid, which, with the remainder of the alcohol, forms ethyl nitrite, $C_2H_5NO_2$, together with other products; but by adding urea to the liquid, which decomposes the nitrous acid as fast as it is formed, this action may be prevented, and the alcohol and nitric acid then form ethyl nitrate. The experiment is most safely conducted on a small scale, and the distillation must be stopped when seven-eighths of the whole have passed over; a little water added to the distilled product separates the nitric ether. Nitric ether has a density of 1·112; it is insoluble in water, has an agreeable sweet taste and odor, and is not decomposed by an aqueous solution of caustic potash, although that substance dissolved in alcohol attacks it even in the cold, with production of potassium nitrate. Its vapor is apt to explode when strongly heated.

Ethyl Nitrite, C_2H_5ONO.—*Nitrous ether.*—Pure nitrous ether can only be obtained by the direct action of the acid itself upon alcohol. 1 part of starch and 10 parts of nitric acid are gently heated in a capacious retort or flask, and the vapor of nitric acid thereby evolved is conducted into alcohol mixed with half its weight of water, contained in a two-necked bottle, which is to be plunged into cold water and connected with a good condensing arrangement. All elevation of temperature must be carefully avoided. The product of this operation is a pale-yellow volatile liquid, having an exceedingly agreeable odor of apples: it boils at 16·4° C. (61° F.), and has a density of 0·947. It is decomposed by potash, without darkening, into potassium nitrite and alcohol.

Nitrous ether, but contaminated with aldehyde, may be prepared by the following simple method. Into a tall cylindrical bottle or jar are to be introduced successively 9 parts of alcohol of sp. gr. 0·830, 4 parts of water, and 8 parts of strong fuming nitric acid; the two latter are added by means of a long funnel with a very narrow orifice, reaching to the bottom of the bottle, so that the contents may form three distinct strata, which slowly mix from the solution of the liquids in each other. The bottle is then loosely stopped, and left two or three days in a cool place, after which it is found to contain two layers of liquid, of which the uppermost is nitrous ether. It is purified by rectification. A somewhat similar product may be obtained by carefully distilling a mixture of 3 parts rectified spirit and 2 of nitric acid of 1·28 sp. gr.: the fire must be withdrawn as soon as the liquid boils.

The *sweet spirits of nitre* of pharmacy, prepared by distilling three pounds of alcohol with four ounces of nitric acid, is a solution of nitrous ether, aldehyde, and perhaps other substances, in spirits of wine.

Ethyl Sulphates.—There are two of these ethers, corresponding to the methyl sulphates.

Acid Ethyl sulphate, *Ethylsulphuric acid* or *Sulphovinic acid*, $C_2H_6SO_4 = C_2H_5OSO_3H = SO_2(OC_2H_5)(OH) = SO_4(C_2H_5)H$, which has the composition of sulphuric acid, SO_4H_2, with half the hydrogen replaced by ethyl, is formed by the action of sulphuric acid upon alcohol. To prepare it, strong rectified spirit of wine is mixed with twice its weight of concentrated sulphuric acid; the mixture is heated to its boiling point, and then left to cool. When cold, it is diluted with a large quantity of water, and neutralized

with chalk, whereby much calcium sulphate is produced. The mass is placed upon a cloth filter, drained, and pressed; and the clear solution is evaporated to a small bulk by the heat of a water-bath, filtered from a little sulphate, and left to crystallize: the product is *calcium ethylsulphate*, in beautiful, colorless, transparent crystals, containing $(SO_4)_2(C_2H_5)_2Ca''.2OH_2$. They dissolve in an equal weight of cold water, and effloresce in a dry atmosphere.

Barium ethylsulphate, $(SO_4)_2(C_2H_5)Ba''.2OH_2$, equally soluble, and still more beautiful, may be produced by substituting, in the above process, barium carbonate for chalk: from this substance the acid may be procured by exactly precipitating the base with dilute sulphuric acid, and evaporating the filtered solution in a vacuum at the temperature of the air. It forms a sour, syrupy liquid, in which sulphuric acid cannot be recognized by the ordinary reagents, and is very easily decomposed by heat, and even by long exposure in the vacuum of the air-pump. All the ethylsulphates are soluble; the solutions are decomposed by ebullition. The lead-salt resembles the barium-compound. The *potassium salt*, $SO_4(C_2H_5)K$—easily made by decomposing calcium ethylsulphate with potassium carbonate—is anhydrous, permanent in the air, very soluble, and crystallizes well.

Potassium ethylsulphate distilled with concentrated sulphuric acid, gives ether; with dilute sulphuric acid, alcohol; and with strong acetic acid, acetic ether. The ethylsulphates heated with calcium or barium hydrate, yield a sulphate of the base and alcohol.

Isethionic acid, $C_2H_6SO_4$, an acid isomeric with ethylsulphuric acid, is obtained, as already observed, by boiling ethionic acid (p. 518) with water; also by the prolonged action of strong sulphuric acid or sulphuric oxide on alcohol or ether, and is found among the residues of the preparation of ether. It is a viscid, strongly acid liquid, which decomposes acetates and common salt, bears without decomposition a heat of 150° C. (302° F.), but blackens at a higher temperature.

The metallic *isethionates* are soluble and crystallizable, and are distinguished from the ethylsulphates, with which they are isomeric, by their much greater stability, most of them sustaining, without alteration, a temperature of 200° C. (392° F.).

Potassium isethionate, $C_2H_5KSO_4$, distilled with phosphorus pentachloride, yields *isethionic chloride*, $C_2H_4SO_2Cl_2$; and this compound, heated in sealed tubes with *ammonia*, is converted into *taurin*, a neutral crystallizable substance likewise obtained from bile:

$$\underset{\text{Isethionic chloride.}}{C_2H_4SO_2Cl_2} + NH_3 + OH_2 = 2HCl + \underset{\text{Taurin.}}{C_2H_7NSO_3}.$$

Taurin, treated with nitrous acid, is reconverted into isethionic acid.

Neutral Ethyl sulphate, $SO_4(C_2H_5)_2$, or $SO_2(OC_2H_5)_2$, is formed by passing the vapor of sulphuric oxide into perfectly anhydrous ether. A syrupy liquid is produced, which, when shaken with 4 vols. of water and 1 vol. of ether, separates into two layers, the lower containing ethylsulphuric acid and various other compounds, while the upper layer consists of an ethereal solution of neutral ethyl sulphate. At a gentle heat the ether is volatilized, and the ethyl sulphate remains as a colorless liquid. It cannot be distilled without decomposition.

Ethyl Sulphites.—The *acid sulphite*, or *Ethylsulphurous acid*, $SO_3(C_2H_5)H$, is produced by the action of nitric acid on ethyl sulphhydrate or sulphocyanate. When concentrated by evaporation it is a heavy oil of specific gravity 1·30. It is a monobasic acid, forming crystallizable salts, which decompose when heated, giving off sulphurous oxide.—*Neutral Ethyl sulphite*, $SO_3(C_2H_5)_2$, is obtained by adding absolute alcohol in excess to chlorine

bisulphide (p. 203). Hydrochloric acid is evolved, and sulphur deposited, while the ethyl sulphite distils as a limpid strongly-smelling liquid, of sp. gr. 1·085, boiling at 170°; it is slowly decomposed by water.

Ethyl Phosphates.—Three ethyl orthophosphates have been obtained, two acid and one neutral, analogous in composition to the sodium phosphates; also a neutral pyrophosphate.

Monethylic phosphate, or *Ethylphosphoric acid*, $PO_4(C_2H_5)H_2$, or $(PO)'''(OC_2H_5)(OH)_2$, also called *Phosphovinic acid*. This acid is bibasic. Its barium salt is prepared by heating to 82° C. (180° F.) a mixture of equal weights of strong alcohol and syrupy phosphoric acid, diluting this mixture, after the lapse of 24 hours, with water, and neutralizing with barium carbonate. The solution of ethylphosphate, separated by filtration from the insoluble phosphate, is evaporated at a moderate temperature. The salt crystallizes in brilliant hexagonal plates, which have a pearly lustre, and are more soluble in cold than in hot water; it dissolves in 15 parts of water at 20° C. (68° F.). The crystals contain $PO_4(C_2H_5)Ba'' . 6OH_2$. From this salt the acid may be obtained by precipitating the barium with dilute sulphuric acid, and evaporating the filtered liquid in the vacuum of the air-pump: it forms a colorless, syrupy liquid, of intensely sour taste, sometimes exhibiting appearances of crystallization. It is very soluble in water, alcohol, and ether, and easily decomposed by heat when in a concentrated state. The ethylphosphates of calcium, silver, and lead possess but little solubility; those of the alkali-metals, magnesium, and strontium, are freely soluble.

Diethylic phosphate, or *Diethylphosphoric acid*, $PO_4(C_2H_5)_2H$, or $(PO)'''(O_2C_2H_5)_2(OH)$, is a monobasic acid, obtained, together with the preceding, by the action of syrupy phosphoric acid upon alcohol. Its barium, silver, and lead-salts are more soluble than the methylphosphates. The calcium salt, $(PO_4)_2(C_2H_5)_4Ca''$, and the lead-salt, $(PO_4)_2(C_2H_5)_2Pb''$, are anhydrous.

Triethylic phosphate, $PO_4(C_2H_5)_3$, or $(PO)'''(OC_2H_5)_3$, is obtained in small quantity by heating the lead-salt of diethylphosphoric acid to 100°, more easily by the action of ethyl-iodide on triargentic phosphate, or of phosphorus oxychloride on sodium ethylate:

$$3C_2H_5ONa + (PO)'''Cl_3 = 3NaCl + (PO)'''(OC_2H_5)_3.$$

It is a limpid liquid of sp. gr. 1·072 at 12° C. (54° F.), boiling at 215° C. (129° F.), soluble in alcohol and ether, and also in water, by which however it is slowly decomposed.

Tetrethylic Pyrophosphate, $P_2O_7(C_2H_5)_4$, produced by the action of ethyl iodide on argentic pyrophosphate, is a viscid liquid of sp. gr. 1·172 at 17° C. (63° F.), decomposed by potash, with formation of potassium diethylphosphate.

Ethyl Borates.—Three of these ethers are known, viz.:

Triethylic borate .	$(C_2H_5)_3BO_3$,
Monethylic borate .	$C_2H_5BO_2$,
Ethylic anhydroborate, or biborate . .	$2C_2H_5BO_2 . B_2O_3$.

Triethylic borate is formed by the action of boron trichloride on alcohol:

$$3C_2H_5(OH) + BCl_3 = 3HCl + (C_2H_5)_3BO_3.$$

It is a thin limpid liquid, of agreeable odor, sp. gr. 0·885, boiling at 119° C. (246° F.), decomposed by water. Its alcoholic solution burns with a fine green flame, throwing off a thick smoke of boric acid.

Monethylic borate, $C_2H_5BO_2$, is formed, with separation of boric acid, by the action of alcohol on the anhydroborate:

$$2C_2H_5BO_2 . B_2O_3 + C_2H_5(OH) = HBO_2 + 3C_2H_5BO_2.$$

It is a colorless, mobile liquid, resembling triethylic borate. The *anhydroborate*, $2C_2H_5BO_2 . B_2O_3$, is formed by the action of boric oxide on an equal weight of anhydrous alcohol, and may be obtained by concentration, in the form of a viscid liquid, which solidifies at 300° C. (572° F.), giving off alcohol vapor and ethene gas, and leaving boric oxide.

Ethyl Silicates. — *Tetrethylic silicate*, $(C_2H_5)_4SiO_4$, or $Si^{iv}(OC_2H_5)_4$, is produced by treating silicic chloride with a small quantity of anhydrous alcohol:

$$4C_2H_5OH + SiCl_4 = 4HCl + Si(OC_2H_5)_4.$$

It is a colorless liquid, having a rather pleasant ethereal odor, and strong peppery taste; sp. gr. 0·993 at 20°. It boils without decomposition between 166° and 160° C. (329°–330° F.), and when set on fire burns with a dazzling flame, diffusing a white smoke of finely divided silica. It is decomposed slowly by water, quickly by ammonia and the fixed alkalies.

Diethylic silicate, $(C_2H_5)_2SiO_3$, or $(SiO)''(OC_2H_5)_2$, is produced, according to Ebelmen,* by the action of silicic chloride on aqueous alcohol:

$$2C_2H_5OH + OH_2 + SiCl_4 = 4HCl + (SiO)(OC_2H_5)_2.$$

It is a colorless liquid, of sp. gr. 1·079, boiling at 350° C. (662° F.), decomposed by water, with separation of silica. On distilling it with a small quantity of aqueous alcohol, a liquid remains in the retort consisting of diethylic disilicate, $(C_2H_5)_2Si_2O_5$, or $(C_2H_5)_2SiO_3 . SiO_2$.

Hexethylic disilicate, $(C_2H_5)_6Si_2O_7$, or $6(C_2H_5)_4SiO_4 . 2SiO_2$. — Friedel and Crafts† were not able to obtain the two ethylic silicates last mentioned; but having prepared a considerable quantity of tetrethylic silicate with alcohol that was not quite anhydrous, they found that the greater part of the product distilled over toward 240°, and that it was not possible, by distillation under the ordinary atmospheric pressure, to obtain a product of definite boiling point. By distillation in a vacuum, however (under a pressure of 3 to 5 millimetres), they obtained, after eight fractionations, a product boiling between 125° and 130° C. (257°–266° F.), and having the composition of *hexethylic disilicate*. This ether is a slightly oily liquid, having a rather fragrant odor, like that of tetrethylic silicate, and a specific gravity of 1·0196 at 0°.

Silicic ethers containing ethyl and methyl, and ethyl and amyl, have likewise been obtained.

The ethylic ethers of organic acids (carbon acids) will be described in connection with those acids.

Ethyl Sulph-hydrate, or **Mercaptan**, C_2H_5SH. — This compound, the sulphur analogue of ethyl alcohol, is produced analogously to methyl sulph-hydrate (p. 515), by the action of potassium sulph-hydrate on calcium ethylsulphate. A solution of caustic potash of sp. gr. 1·28 or 1·3, is saturated with sulphuretted hydrogen, and mixed in a retort with an equal volume of solution of calcium ethylsulphate of the same density. The retort is connected with a good condenser, and heat is applied by means of a bath of salt and water. Mercaptan and water distil over together, and are easily separated by a tap-funnel. The product thus obtained is a colorless, limpid liquid, of sp. gr. 0·842, but slightly soluble in water, easily miscible, on the contrary, with alcohol. It boils at 36° C. (96° F.). The vapor of mercaptan has a most intolerable odor of onions, which adheres to the clothes and person with great obstinacy: it is very inflammable, and burns with a blue flame.

When mercaptan is brought into contact with mercuric oxide, even in

* Ann. Chim. Phys. [3] xvi. 144. † Ann. Chim. Phys. [4] ix. 5.

the cold, violent reaction ensues, water is formed, and a white substance is produced, soluble in alcohol, and separating from that liquid in distinct crystals which contain $(C_2H_5)_2S_2Hg''$. This compound is decomposed by sulphuretted hydrogen, mercuric sulphide being thrown down, and mercaptan reproduced. By adding solutions of lead, copper, silver, and gold to an alcoholic solution of mercaptan, corresponding compounds containing those metals are formed. Caustic potash produces no effect upon mercaptan, but potassium displaces hydrogen, and gives rise to a crystallizable compound, C_2H_5SK, soluble in water. Sodium acts in a similar manner.

Ethyl Sulphides. — Three of these compounds have been obtained, analogous in composition to the methyl sulphides, and produced by similar reactions. The *monosulphide*, $(C_2H_5)S$, or $C_2H_5SC_2H_5$, is a colorless oily liquid, having a very pungent alliaceous odor, a specific gravity of 0·825 at 20° C. (68° F.), and boiling at 72° C. (162° F.). It is very inflammable, and burns with a blue flame. When poured into chlorine gas, it takes fire; but when dry chlorine is passed into a flask containing it, not at first into the liquid, the vessel being kept cool and in the shade, substitution-products are formed and hydrochloric acid is copiously evolved. The product consists chiefly of *dichlorethylic sulphide*, $(C_2H_4Cl)_2S$. If the action takes place in diffused daylight, and without external cooling, the compounds $(C_2H_2Cl_3)_2S$ and $(C_2HCl_4)_2S$ are obtained, which may be separated by fractional distillation, the first boiling between 189° and 192° C. (372°–378° F.), the second between 217° and 222° C. (423–432° F.). The action of chlorine on ethyl sulphide in sunshine yields a more highly chlorinated compound, probably $(C_2Cl_5)_2S$.

Ethyl bisulphide, $(C_2H_5)_2S_2$, obtained by distilling potassium bisulphide with potassium ethylsulphate or with ethyl oxalate, is a colorless oily liquid, very inflammable, boiling at 151° C. (302° F.). The *trisulphide*, $(C_2H_5)_2S_3$, is a heavy oily liquid, obtained by acting in like manner on potassium pentasulphide.

Triethylsulphurous Compounds.* — When ethyl monosulphide and ethyl iodide are heated together, they unite and form *sulphurous iodotriethide*, $(C_2H_5)_2S \cdot C_2H_5I$, or $S^{iv}(C_2H_5)_3I$, which crystallizes in needles. The same compound is formed by the action of ethyl iodide on ethyl sulph-hydrate:

$$2C_2H_5I + C_2H_5SH = HI + S(C_2H_5)_3I,$$

or of hydrogen iodide on ethyl monosulphide:

$$HI + 2(C_2H_5)_2S = C_2H_5SH + S(C_2H_5)_3I.$$

Sulphurous iodotriethide is insoluble in ether, slightly soluble in alcohol, and crystallizes from the solution in white deliquescent needles belonging to the monoclinic system. It unites with metallic chlorides.

Ethyl chloride and ethyl bromide unite in like manner, but less readily, with ethyl sulphide, forming the compounds $S(C_2H_5)_3Cl$ and $S(C_2H_5)_3Br$, both of which crystallize in needles.

By treating the iodine compound with recently-precipitated silver oxide, a strongly alkaline solution is obtained, which dries up over oil of vitriol to a crystalline deliquescent mass, consisting of *sulphurous triethyl-hydroxylate*, $(C_2H_5)_3S(OH)$. The solution of this substance dissolves the skin like caustic potash, and forms similar precipitates with various metallic salts. It neutralizes acids, forming definite crystallizable salts, *e.g.*, the *nitrate*, $(C_2H_5)_3SONO_2$, the *acetate* $(C_2H_5)_3S(OC_2H_3O)$, &c.

The formulæ of these compounds show that sulphur is at least quadrivalent (p. 237).

* *A. von Oefele*, Chem. Soc. Journal, xvii. 108. *Cahours*, Ann. Ch. Pharm. cxxxv. 352; cxxxvi. 151. *Dehn*, Ann. Ch. Pharm. Suppl. iv. 83.

PROPYL ALCOHOLS AND ETHERS.

It has already been observed that the three-carbon alcohol, C_3H_8O, is susceptible of two isomeric modifications, namely:

Normal Propyl alcohol $C\begin{cases} CH_2CH_3 \\ H_2 \\ OH \end{cases}$ or $\begin{matrix} CH_3 \\ | \\ CH_2 \\ | \\ CH_2OH \end{matrix}$ thus

Isopropyl alcohol $C\begin{cases} CH_3 \\ CH_3 \\ H \\ OH \end{cases}$ or $\begin{matrix} H_3C\ CH_3 \\ \vee \\ HCOH \end{matrix}$

each of which may give rise to a corresponding set of ethers and other derivatives. The normal propyl compounds, however, are but little known, none of them having yet been prepared synthetically, except propylamine and propyl cyanide, to be afterwards considered. Chancel, in 1853, by subjecting the fusel-oil of marc brandy, prepared in the south of France, to fractional distillation, obtained a number of alcohols, among which was one to which he assigned the composition C_3H_8O; this has usually been regarded as normal propyl alcohol, but it was not obtained pure, and is altogether very little known.

Isopropyl Alcohol, $CH(CH_3)_2OH$. — This alcohol is prepared: 1. From acetone, $(CO)''(CH_3)_2$, by direct addition of hydrogen, evolved by the action of water on sodium amalgam:

$$\begin{matrix} H_3C\ CH_3 \\ \vee \\ CO \\ \text{Acetone.} \end{matrix} + H_2 = \begin{matrix} H_3C\ CH_3 \\ \vee \\ HCOH \\ \text{Isopropyl alcohol.} \end{matrix}$$

This mode of synthesis affords direct proof of the constitution of isopropylic alcohol, the addition of the two hydrogen-atoms being tantamount to the replacement of the bivalent radical oxygen by the two monad radicals, hydrogen and hydroxyl.

2. Isopropyl iodide is prepared by the action of iodine and phosphorus on glycerin; this iodide is easily converted into the oxalate or acetate by treatment with silver oxalate or acetate; and from either of these ethers the alcohol may be obtained by distillation with potash or soda.

Isopropyl alcohol is a colorless, not very mobile liquid, having a peculiar odor, a specific gravity of 0·791 at 15° C. (60° F.), boiling at 83° to 84° C. (181°–183° F.), under a barometric pressure of 739 millimetres, not freezing at 20°. It does not act on polarized light. It is very difficult to dry, as it mixes with water in all proportions, and forms with it three definite and very stable hydrates, viz., $3C_3H_8O.2OH_2$, boiling at 78°–80° C. (172°–176° F.); $2C_3H_8O.OH_2$, boiling at 80°; and $3C_3H_8O.OH_2$, boiling at 81°. The second of these hydrates exhibits a very close resemblance to ethyl alcohol, and has the same percentage composition, boils at nearly the same temperature, and likewise yields acetic acid by oxidation (see p. 532); moreover it retains its water of hydration so obstinately, that it does not even change the white color of anhydrous cupric sulphate to blue. The readiest mode of distinguishing between this hydrate and ethyl alcohol is to submit

them to the action of iodine and phosphorus, whereby the former is converted into isopropyl iodide, the latter into ethyl iodide.

The characteristic property of isopropyl alcohol is that it yields acetone by oxidation with dilute chromic acid, this transformation being the reverse of that by which it is produced:

$$\begin{matrix} H_3C\ CH_3 \\ \diagdown\diagup \\ HCOH \end{matrix} + O = \begin{matrix} H_3C\ CH_3 \\ \diagdown\diagup \\ CO \end{matrix} + OH_2$$

On pushing the oxidation further, the acetone breaks up into acetic acid, carbon dioxide and water:

$$\underset{\text{Acetone.}}{CO(CH_3)_2} + O_4 = \underset{\text{Acetic acid.}}{CO(CH_3)OH} + CO_2 + OH_2$$

The evolution of carbon dioxide in this reaction affords a further distinction between hydrated isopropyl alcohol and ethyl alcohol.

The formation of a ketone by oxidation is the essential characteristic of a secondary alcohol, and is an immediate consequence of its structure. The primary alcohols, $C_nH_{2n+2}O$, are directly converted by oxidation into aldehydes, $C_nH_{2n}O$, and acids, $C_nH_{2n}O_2$, not into ketones; thus:

$$\underset{\text{Ethyl alcohol.}}{\begin{matrix} CH_3 \\ | \\ CH_2OH \end{matrix}} + O = OH_2 + \underset{\text{Aldehyde.}}{\begin{matrix} CH_3 \\ | \\ H{-}C{=}O \end{matrix}}$$

$$\underset{\text{Aldehyde.}}{C_2H_4O} + O = \underset{\text{Acetic acid.}}{C_2H_4O_2}$$

Isopropyl alcohol, heated with acetic acid, or with potassium acetate and sulphuric acid, is converted into *isopropyl acetate*, $CH(CH_3)_2OC_2H_3O$.

Isopropyl Iodide, $CH(CH_3)_2I$, is most conveniently prepared by the action of hydriodic acid, concentrated and in larger excess, on glycerin (propenyl alcohol) $C_3H_8O_3$:

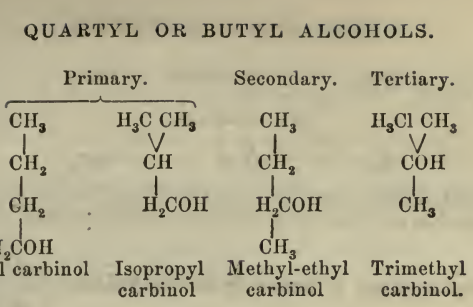
$$C_3H_8O_3 + 5HI = C_3H_7I + 3OH_2 + 2I_2.$$

The iodine, as fast as it is set free by the reaction, may be reconverted into hydriodic acid by means of phosphorus, and will then be ready to act upon another portion of glycerin. It may also be produced by the action of hydriodic acid on isopropyl alcohol, allyl iodide, C_3H_5I, propene, or propene alcohol.

Isopropyl iodide is an oil boiling at 89°–90° C. (192°–194° F.), and having a specific gravity of 1·70. With *sodium* in presence of ether it yields propene, propane, and di-isopropyl, C_6H_{14}. *Bromine* expels the iodine and forms isopropyl bromide.

QUARTYL OR BUTYL ALCOHOLS AND ETHERS.

Theory indicates the existence of four alcohols included in the formula $C_4H_{10}O$, two primary, one secondary, and one tertiary; thus,



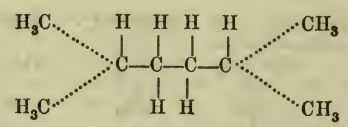
Propyl Carbinol, $C\begin{cases}CH_2CH_2CH_3\\H_2\\OH\end{cases}$.—This alcohol is obtained from quartyl chloride, C_4H_9Cl (produced by the action of chlorine or quartane or diethyl, $C_{14}H_{10}$), by heating that chloride with potassium acetate and strong acetic acid, whereby it is converted into quartyl acetate, and treating that compound with barium hydrate. The alcohol thus prepared yields butyric acid by oxidation.*

Isopropyl Carbinol, $C\begin{cases}CH(CH_3)_2\\H_2\\OH\end{cases}$.—This variety of primary butyl-alcohol was found by Wurtz in the fusel-oil obtained by fermenting the molasses of beet-root sugar. To separate it, this oil is submitted to fractional distillation, and the liquid boiling between 108° and 118° is repeatedly rectified over potassium hydrate, till it boils constantly at 110° C. (230° F.).

Pure isopropyl carbinol is a colorless liquid, having an odor somewhat like that of amyl alcohol, but less pungent, and more vinous: sp. gr. = 0·8032 at 18·5° C. (65° F.). It dissolves in 10½ times its weight of water, and is separated therefrom, as an oil, by calcium chloride, sodium chloride, and other soluble salts. By oxidation it is converted into butyric acid, $C_4H_8O_2$, whence it appears to be a primary alcohol. Formerly also this alcohol was assumed to have the constitution represented by the first of the formulæ above given; in other words, to consist of *propyl-carbinol*, $CH_2(C_3H_7)OH$; and all the other alcohols of the series produced by fermentation were supposed to be similarly constituted. This assumption, however, did not rest on very exact experimental data; and from recent experiments by Erlenmeyer,† it appears that butyl alcohol produced by fermentation consists of *isopropyl-carbinol*, $CH_2[CH(CH_3)_2]OH$, or is represented by the second of the formulæ above given for the primary four-carbon alcohol.

Isopropyl-carbinol is acted upon by acids and other chemical reagents much in the same manner as common alcohol (methyl-carbinol). With strong *sulphuric acid* it yields *quartyl-sulphuric acid*, $SO_4H(C_4H_9)$, if the mixture is kept cool; but on heating the liquid *quartene*, or *butylene*, C_4H_8 is given off mixed with sulphurous oxide and carbon dioxide. Heated with *hydrochloric acid* in a sealed tube, or treated with *phosphorus pentachloride* or *oxychloride*, it is converted into *quartyl chloride*, C_4H_9Cl, or *chloroquartane*, an ethereal liquid, having a pungent odor, and boiling at 70° C. (158° F.); *quartyl bromide*, C_4H_9Br, obtained in like manner, boils at 89°, the *iodide* C_4H_9I, at 121° C. (250 F.). The iodide is decomposed by potassium or sodium, yielding *diquartyl* or *dibutyl*, C_8H_{18}, probably:

* *Schüyen*, Ann. Ch. Pharm. cxxx., 233.
† Zeitschrift für Chemie, Neue Reihe, iii. 117. The details of the investigation are not yet published.



a limpid liquid, lighter than water, and boiling at 105° C. (221° F.). The same hydrocarbon is obtained by the electrolysis of valeric acid, $C_5H_{10}O_2$.

Methyl-ethyl Carbinol, or Secondary Butylic Alcohol,—$C\left\{\begin{matrix}CH_3\\C_2H_5\\H\\OH\end{matrix}\right.$. — This alcohol is obtained from erythrite (*erythromannite*), a saccharine substance having the composition of a tetratomic alcohol, $C_4H_{10}O_4$, or $C_4H_6(OH)_4$. The erythrite, distilled with fuming hydriodic acid, yields methyl-ethyl-iodomethane, or secondary butyl iodide, $C(CH_3)(C_2H_5)HI$, and this liquid, treated with moist silver oxide, is converted into methyl-ethyl carbinol:

$C(CH_3)(C_2H_5)HI$	+	$AgOH$	=	AgI	+	$C(CH_3)(C_2H_5)HOH.$
Methyl-ethyl iodomethane.		Silver hydrate.		Silver iodide.		Methyl-ethyl-carbinol.

Methyl-ethyl carbinol is a colorless oily liquid, having a strong odor and burning taste, a specific gravity of 0·85 at 0°, and boiling at 95°–98° C. (203°–208° F.) (about 10° C. (18° F.) lower than the primary alcohol). When heated to 250° C. (482° F.), it is for the most part resolved into water and quartene or butylene: $C_4H_{10}O = OH_2 + C_4H_8$.

Methyl-ethyl Iodomethane, or *Secondary Butyl iodide*, prepared as above, or by the action of strong hydriodic acid on the alcohol, is a liquid having a pleasant ethereal odor, a specific gravity of 1·632 at 0°, 1·600 at 20° C. (68° F.) and 1·584 at 30° C. (86° F.). It boils at 118° C. (244° F.). Bromine decomposes it, expelling the iodine and forming quartene dibromide $C_4H_8Cl_2$. When distilled with alcoholic potash it gives off quartene. This tendency to give off the corresponding olefine is characteristic of all the secondary alcohols and ethers, as will be further noticed in connection with the five-carbon compounds.

Trimethyl Carbinol or Tertiary Butyl Alcohol, $C\left\{\begin{matrix}(CH_3)_3\\OH\end{matrix}\right.$, is produced by treating zinc methide with carbonyl chloride (phosgene gas) or acetyl chloride, and submitting the product to the action of water.*

$2COCl_2$	+	$Zn(CH_3)_2$	=	$ZnCl_2$	+	$2COCH_3Cl$
Carbonyl chloride.		Zinc methide.		Zinc. chloride.		Acetyl chloride.

$COCH_3Cl$	+	$Zn(CH_3)_2$	=	ZnO	+	$C\left\{\begin{matrix}(CH_3)_3\\Cl\end{matrix}\right.$
Acetyl chloride.		Zinc methide.		Zinc. oxide.		Trimethyl chloromethane.

$C\left\{\begin{matrix}(CH_3)_3\\Cl\end{matrix}\right.$	+	HOH	=	HCl	+	$C\left\{\begin{matrix}(CH_3)_3\\OH\end{matrix}\right.$
Trimethyl-chloromethane.		Water.				Trimethyl carbinol.

When acetyl chloride is used, the formation of trimethyl-chloromethane takes place by a very simple reaction. In the case of carbonyl chloride it

* *Buttlerow*, Zeitschrift für Chem. und Pharm. 1864, pp. 385, 702.

takes place by two stages, the first of which is the production of acetyl chloride. The other tertiary alcohols, to be noticed hereafter, are obtained by similar series of reactions.

The properties of this, and of the other tertiary alcohols, have not been much studied. They are distinguished from the primary and secondary alcohols by the products which they yield with oxidizing agents. Primary alcohols of the series $C_nH_{2n+2}O$, oxidizing with chromic acid, yield, as already observed, the corresponding acids, $C_nH_{2n}O_2$; secondary alcohols, the corresponding ketones. Tertiary alcohols, on the other hand, are split up by oxidation, yielding bodies containing a smaller number of carbon-atoms: thus, trimethyl carbinol is converted by oxidizing agents into formic and propionic acids:

$$\underset{\text{Trimethyl carbinol.}}{C_4H_{10}O} + O_4 = \underset{\text{Formic acid.}}{CH_2O_2} + \underset{\text{Propionic acid.}}{C_3H_6O_2} + OH_2$$

QUINTYL OR AMYL ALCOHOLS AND ETHERS.

The formula $C_5H_{10}O$ may include six different alcohols: two primary, three secondary, and one tertiary, viz.:

Primary $C\begin{cases}CH_2CH_2CH_2CH_3\\H\\H\\OH\end{cases}$ Butyl carbinol. and $C\begin{cases}CH_2CH(CH_3)_2\\H\\H\\OH\end{cases}$ Isobutyl carbinol.*

Secondary $C\begin{cases}CH_2CH_2CH_3\\CH_3\\H\\OH\end{cases}$ Methyl-propyl carbinol. $C\begin{cases}CH(CH_3)_2\\CH_3\\H\\OH\end{cases}$ Methyl-isopropyl carbinol. and $C\begin{cases}CH_2CH_3\\CH_2CH_3\\H\\OH\end{cases}$ Diethyl carbinol.

Tertiary $C\begin{cases}CH_2CH_3\\CH_3\\CH_3\\OH\end{cases}$ Dimethyl-ethyl carbinol.

Of these, however, only two have been distinguished with certainty, viz., a primary alcohol, produced by fermentation, and a secondary alcohol obtained from the corresponding olefine, namely, quintene or amylene.

Isobutyl Carbinol, $CH_2(C_4H_9)OH$. — This, according to Erlenmeyer, is the ordinary amyl alcohol produced by fermentation. In the manufacture of brandy from corn, potatoes, or the must of grapes, the ethyl alcohol is found to be accompanied by an acrid oily liquid called *fusel-oil*, which is very difficult to separate completely from the ethyl alcohol. It passes over, however, in considerable quantity towards the end of the distillation, and may be collected apart, washed by agitation with several successive portions of water to free it from ethyl alcohol, and re-distilled. The liquid thus obtained consists chiefly of amyl alcohol, sometimes mixed with propylic, butylic, and other alcohols. The amyl alcohol may be obtained pure by fractional distillation, the portion which passes over between 128° and 132° C. (262°–270° F.) being collected apart. Potato fusel-oil consists almost wholly of ethyl and amyl alcohols, the latter constituting the greater quantity.

* The four-carbon radical derived from methyl by substitution of isopropyl for one atom of hydrogen may be called isoquartyl or isobutyl.

Amyl alcohol is an oily, colorless, mobile liquid, having an odor peculiar to itself, and a burning acrid taste. Its vapor when inhaled produces coughing and oppression of the chest. Its specific gravity is 0·8111. When dropped on paper it forms a greasy stain, which, however, disappears after a while. It is not perceptibly soluble in water, but floats on the surface of that liquid like an oil; common alcohol, ether, and various essential oils dissolve it readily.

Amyl alcohol usually exerts a rotatory action on polarized light, but the rotatory power varies considerably in different samples. Pasteur, indeed, has shown that ordinary amyl alcohol is a mixture of two isomeric alcohols, having the same vapor-density, but differing in their optical properties, one of them turning the plane of polarization to the right, whereas the other is optically inactive. They are separated by converting the crude amyl alcohol into amylsulphuric acid, saturating with barium carbonate, and crystallizing the barium amyl sulphate thus formed. The salt obtained from the active amyl alcohol is $2\frac{1}{2}$ more soluble than that obtained from the inactive alcohol, and consequently the latter crystallizes out first; and by precipitating the barium from the solution of either salt with sulphuric acid, and distilling the amylsulphuric acid thus separated with water, the corresponding amyl alcohol is obtained. The difference of optical character between the two alcohols — which is traceable through many of their derivatives — has not been satisfactorily explained; but it probably depends upon the arrangement of the molecules, rather than upon that of the atoms within the molecule.

Vapor of amyl alcohol passed through a red-hot tube, yields a mixture of ethene, propene, quartene, and quintene or amylene.

Amyl alcohol takes fire easily and burns with a blue flame. When exposed to the air in contact with platinum black, it is oxidized to valeric acid, $C_5H_{10}O_2$. The same acid is obtained by heating amyl alcohol with a mixture of *potassium bichromate* and *sulphuric acid*.

$$\underset{\text{Amyl alcohol.}}{CH_2(C_4H_9)OH} + O_3 = OH_2 + \underset{\text{Valeric acid.}}{CO(C_4H_9)OH.}$$

Amyl alcohol, heated to 220° C. (423° F.) with a mixture of *potassium hydrate* and *lime*, is converted into valeric acid, with evolution of hydrogen:

$$\underset{\text{Amyl alcohol.}}{C_5H_{12}O} + KHO = \underset{\text{Potassium valerate.}}{C_5H_9KO_2} + H_2.$$

Potassium and *sodium* dissolve in amyl alcohol as in ethyl alcohol, yielding the compound, $C_5H_{11}KO$, and $C_5H_{11}NaO$, which, when treated with amyl iodide, yield *amyl oxide* or *amyl ether*, $(C_5H_{11})_2O$; and with ethyl iodide, *ethyl-amyl oxide*, $(C_2H_5)(C_5H_{11})O$.

Chlorine acts upon amyl alcohol as upon ethyl alcohol, excepting that it finally removes only four atoms of hydrogen, instead of five:

$$\underset{\text{Amyl alcohol.}}{C_5H_{12}O} + 3Cl_2 = 4HCl + \underset{\text{Chloramylal.}}{C_5H_8Cl_2O.}$$

Amyl alcohol is acted upon by acids, like common alcohol, yielding ethers. When mixed with strong *sulphuric acid*, it is converted into amylsulphuric acid, $(C_5H_{11})HSO_4$; and, on distilling the mixture, amyl oxide, $(C_5H_{11})_2O$, passes over, together with amylene, and several other hydrocarbons.

Amylene, or Quintene, C_5H_{10}, is likewise obtained, together with quintane, C_5H_{12}, and higher homologues of both these bodies, by distilling amyl alcohol with zinc chloride. It is a colorless liquid, having a peculiar and somewhat unpleasant odor; boils at 35° C. (95° F.), and when set on fire,

burns with a bright, very smoky flame. — Vapor of amylene is completely absorbed by antimony pentachloride and sulphuric oxide. — Strong sulphuric acid dissolves amylene, when the two are shaken up together, but the hydrocarbon soon separates as an oily layer, which however consists, not of amylene, but of *diamylene* (*paramylene*), $C_{10}H_{20}$. Amylene unites with hydrochloric, hydrobromic, and hydriodic acid, forming compounds isomeric with amyl chloride, &c.

Amyl Chloride, $C_5H_{11}Cl$, is prepared by distilling equal weights of amyl alcohol and phosphorus pentachloride, washing the product repeatedly with alkaline water, and rectifying it from calcium chloride. Less pure it may be obtained by saturating amyl alcohol with hydrochloric acid. It is a colorless liquid, of agreeable aromatic odor, insoluble in water, and neutral to test-paper: it boils at 102° C. (216° F.), and ignites readily, burning with a flame green at the edges. By the long-continued action of chlorine, aided by powerful sunshine, it is converted into *octochlorinated amyl chloride*, or *nonochloroquintane*, $C_5H_3Cl_9$, a volatile, colorless liquid, smelling like camphor: the whole of the hydrogen has not yet, however, been removed.

Amyl Bromide, $C_5H_{11}Br$, is a volatile, colorless liquid, heavier than water. It is obtained by distilling amyl alcohol, bromine, and phosphorus together. (See ethyl bromide, p. 522.) Its odor is penetrating and alliaceous. The bromide is decomposed by an alcoholic solution of potash, with reproduction of the alcohol and formation of potassium bromide.

Amyl Iodide, $C_5H_{11}I$, is procured by distilling a mixture of 15 parts of amyl alcohol, 8 of iodine, and 1 of phosphorus. It is colorless when pure, heavier than water, volatile without decomposition at 146° C. (295 F.), and in other respects resembles the bromide: it is partly decomposed by exposure to light. Heated to 290° C. (554° F.) in sealed tubes, with zinc, it yields *diamyl*, $C_{10}H_{22}$, or $C_5H_{11}.C_5H_{11}$, a colorless ethereal liquid, boiling at 155° C. (311° F.), and isomeric, or identical with decane (p. 474). At the same time there is formed a compound of zinc iodide with zinc amylide, $Zn(C_5H_{11})_2$, which is decomposed by contact with water, yielding zinc oxide and quintane or amyl hydride (p. 478):

$$Zn(C_5H_{11})_2 + OH_2 = ZnO + 2C_5H_{12}.$$

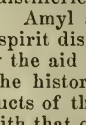
Amyl Oxide, $(C_5H_{11})_2O$, obtained by the processes already mentioned, is a colorless oily liquid, of specific gravity of 0·779°, and boiling at 176°.

Amyl Sulphuric, or Sulphamylic Acid, $(C_5H_{11})HSO_4$, or $C_5H_{11}OSO_3H$. — The barium salt of this acid, $(C_5H_{11})_2Ba''(SO_4)_2 . 2$ aq., prepared like the ethylsulphate (p. 527), crystallizes on evaporating the solution in small brilliant pearly plates; the difference of solubility of the salts prepared from optically active and optically inactive amyl alcohol has already been mentioned. The barium may be precipitated from the salt by dilute sulphuric acid, and the sulphamylic acid concentrated by spontaneous evaporation to a syrupy, or even crystalline state: it has an acid and bitter taste, strongly reddens litmus-paper, and is decomposed by ebullition into amyl alcohol and sulphuric acid. The potassium salt forms groups of small radiated needles, very soluble in water. The sulphamylates of calcium and lead are also soluble and crystallizable.

Amyl sulph-hydrate, $C_5H_{11}SH$, and *Amyl sulphide*, $(C_5H_{11})_2S$, have likewise been obtained: they resemble the ethyl compounds in their properties and reactions.

Fusel-oil or Grain-spirit. — The fusel oil, separated in large quantities from grain-spirit by the London rectifiers, consists chiefly of amyl alcohol

mixed with ethyl alcohol and water. Sometimes it contains in addition more or less of the ethyl- or amyl-compounds of certain fatty acids thought to have been identified with œnanthylic and palmitic acids. These last-named substances form the principal part of the nearly solid fat produced in this manner in whiskey distilleries conducted on the old plan. Mulder has described, under the name of *corn-oil*, another constituent of the crude fusel-oil of Holland: it has a very powerful odor, resembling that of some of the umbelliferous plants, and is unaffected by solution of caustic potash. According to Mr. Rowney, the fusel-oil of the Scotch distilleries contains in addition a certain quantity of capric acid, $C_{10}H_{20}O_2$. Amyl alcohol, in addition to butyl alcohol, has been separated from the spirit distilled from beet-molasses, and from artificial grape-sugar made by the aid of sulphuric acid. Although much obscurity yet hangs over the history of these substances, it is generally supposed that they are products of the fermentation of sugar, and have an origin contemporaneous with that of common alcohol.

Methyl-isopropyl carbinol, $CH(CH_3)[CH(CH_3)_2]'OH$ =  **or Amylene hydrate,** $(C_5H_{10})''\left\{\begin{matrix}H\\OH\end{matrix}\right.$. — This is a secondary alcohol produced from amylene, C_5H_{10}, by combining that substance with hydriodic acid, and decomposing the resulting hydriodide, $C_5H_{10}.HI$, with moist silver oxide, whereby silver iodide and amylene hydrate are obtained:

$$2(C_5H_{10}.HI) + Ag_2O + H_2O = 2AgI + 2[C_5H_{10}.H(OH)].$$

A portion of the hydriodide is at the same time resolved, by the heat evolved in the reaction, into hydriodic acid and amylene; and, on submitting the resulting liquid to fractional distillation, the amylene passes over first, and then, between 105° and 108° C. (221° and 226° F.), the amylene hydrate or methyl-isopropyl carbinol.

This alcohol is a liquid having a specific gravity of 0·829 at 0°, and a pungent ethereal odor, quite distinct from that of ordinary amyl alcohol. Heated with strong *sulphuric acid*, it is converted, not into amylsulphuric acid, but into hydrocarbons polymeric with amylene, viz., diamylene, or decene, $C_{10}H_{20}$, and triamylene, or quindecene, $C_{15}H_{30}$. *Hydriodic acid* converts it, at ordinary temperatures, into amylene hydriodide, $C_5H_{10}.HI$, boiling at 130° C. (266° F.), (amyl iodide at 146° C. [295° F.]). *Hydrochloric acid* converts it (even at 0°) into amylene hydrochloride, $C_5H_{10}.HCl$, having a boiling point 10° C. (18° F.) below that of amyl chloride. On mixing it with two atoms of *bromine* at a very low temperature, a red liquid is formed, which, as soon as it attains the ordinary temperature of the air, is resolved into water and amylene bromide. Heated for some time to 100° C. with strong *acetic acid*, it yields amylene, together with a small quantity of amylene acetate. *Sodium* dissolves in amylene hydrate with evolution of hydrogen, forming a colorless translucent mass, which has the composition $C_5H_{10}NaOH$, and is decomposed by amylene hydriodide in the manner shown by the equation:

$C_5H_{10}NaOH$	+	$C_5H_{10}HI$	=	C_5H_{10}	+	$C_5H_{10}H(OH)$	+	NaI.
Sodium compound.		Amylene hydriodide.		Amylene.		Amylene hydrate.		

From these reactions it is apparent that amylene hydrate or methyl-

isopropyl carbinol is especially distinguished from amyl alcohol or butyl carbinol, by the facility with which it gives up the corresponding olefine. This peculiarity is exhibited also by all the secondary alcohols of the series. These alcohols indeed may be regarded as connecting links between the primary monatomic alcohols and the secondary alcohols, or glycols; *e. g.*:

$C_5H_{11}(OH)$	$C_5H_{10}\left\{\begin{matrix}H\\OH\end{matrix}\right.$	$C_5H_{10}\left\{\begin{matrix}OH\\OH\end{matrix}\right.$
Amyl alcohol.	Amylene hydrate.	Amylene glycol.

SEXTYL, OR HEXYL, ALCOHOLS AND ETHERS.

The number of possible modifications of an alcohol increases with the number of carbon-atoms in its molecular formula. Thus we have seen that there may be two propyl alcohols, C_3H_8O, four butyl alcohols, $C_4H_{10}O$, and six amyl alcohols, $C_5H_{12}O$. The six-carbon formula, $C_6H_{14}O$, will in like manner be found to include ten isomeric alcohols—three primary, four secondary, and three tertiary; but as the manner in which these modifications arise has been sufficiently explained in the preceding pages, the further development of the theoretical formulæ may be left as an exercise for the student.

The number of modifications of the six-carbon alcohol actually known, is five; of which two are primary, one is secondary, and the remaining two are tertiary.

Primary Hexyl Alcohols.—The normal alcohol, or *Amyl-carbinol*, $C_6H_{13}(OH)$, or $C\left\{\begin{matrix}C_5H_{11}\\H_2\\OH\end{matrix}\right.$, is prepared by treating sextane, or hexyl hydride, C_6H_{14}, obtained from American petroleum, with chlorine, converting the resulting hexyl chloride, $C_6H_{13}Cl$, into hexyl acetate, $C_6H_{13}(OC_2H_3O)$, by treatment with silver acetate, and distilling the hexyl acetate with potash. The hexyl alcohol thus prepared boils at about 150° C. (302° F.), and smells like amyl alcohol.

Another primary hexyl alcohol was found by Faget in fusel-oil. The statements respecting it are not very exact, but as it is produced by fermentation, it is probably constituted like ordinary amyl alcohol, and therefore in the manner represented by the formula, $C\left\{\begin{matrix}CH_2CH_2CH(CH_3)_2\\H\\OH\end{matrix}\right.$.

Both these alcohols, when oxidized by chromic acid, yield caproic acid, $C_6H_{12}O_2$.

Secondary Hexyl Alcohol, probably Methyl-isobutyl carbinol, $C\left\{\begin{matrix}CH_2CH(CH_3)_2\\CH_3\\H\\OH\end{matrix}\right.$,

or **Hexylene hydrate,** $C_6H_{12}\left\{\begin{matrix}H\\OH\end{matrix}\right.$.—This alcohol, discovered by Wanklyn and Erlenmeyer,* is produced from mannite, a saccharine body having the composition of a hexatomic alcohol, $C_6H_8(OH)_6$, by treating that substance with a large excess of very strong hydriodic acid, whereby it is converted into secondary hexyl iodide, or hexylene hydriodide, $C_6H_{12}\cdot HI$:

$$C_6H_8(OH)_6 + 11HI = C_6H_{12}HI + 6OH_2 + 5I_2;$$

and digesting this hydriodide with silver oxide and water:

$$C_{12}H_{12}HI + H_2O + Ag_2O = 2AgI + C_6H_{12}H(OH).$$

* Journal of the Chemical Society [2], i. 221.

It is a viscid liquid, having a pleasant, refreshing odor; boils at 137°; has a sp. gr. of 0·8327 at 0°, 0·8209 at 16°, and 0·7482 at 99°, so that it expands somewhat rapidly by heat. Strong hydrochloric acid converts it into the corresponding hydrochloride, $C_6H_{12}HCl$, which boils at 120° C. (248° F.), and yields hexylene when digested at 100° C., with alcoholic potash.

Hexylene hydrate, or methyl-isobutyl carbinol, is converted by oxidation with potassium bichromate and sulphuric acid, into a ketone, $C_6H_{12}O$ = $C\begin{cases} CH_2CH(CH_3)_2 \\ CH_3 \\ O'' \end{cases}$, which does not absorb oxygen from the air; but, when further treated with the oxidizing mixture just mentioned, yields butyric, acetic, and carbonic acids, and water. These reactions show that the alcohol in question is a secondary alcohol.

Tertiary Hexyl Alcohols.—Three of these alcohols are possible, namely:

Methyl-diethyl carbinol $C\begin{cases} CH_3 \\ (C_2H_5)_2 \\ OH \end{cases}$

Propyl-dimethyl carbinol $C\begin{cases} CH_2(C_2H_5) \\ (CH_3)_2 \\ OH \end{cases}$

Isopropyl-dimethyl carbinol $C\begin{cases} CH(CH_3)_2 \\ (CH_3)_2 \\ OH. \end{cases}$

The third has not yet been obtained. The first is prepared by treating zinc ethyl with acetyl chloride, and decomposing the resulting methyl-diethyl-chlorethane, $C\begin{cases} CH_3 \\ (C_2H_5)_2, \\ Cl \end{cases}$ with water; the second by proceeding in like manner with zinc methyl and butyryl chloride, $CO(C_3H_7)Cl$.

SEPTYL, OR HEPTYL, ALCOHOLS AND ETHERS.

Of these compounds only the normal primary alcohol, $C_7H_{15}(OH)$, or *Hexyl carbinol*, $C\begin{cases} C_6H_{13} \\ H_2 \\ OH \end{cases}$, is known with certainty. It is prepared, either by the action of nascent hydrogen (evolved by the action of sodium amalgam on water) on œnanthylic aldehyde (œnanthol):

$$\underset{\text{Aldehyde.}}{C_7H_{14}O} + H_2 = \underset{\text{Alcohol.}}{C_7H_{16}O};$$

or from septane or heptyl hydride, C_7H_{16}, in the same manner as hexyl alcohol from hexyl hydride (p. 539). It is a colorless, oily liquid, insoluble in water; but its properties are not much known.

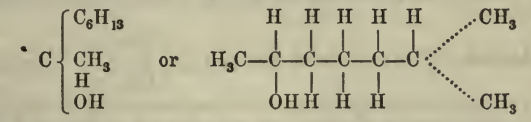
Another heptyl alcohol was separated by Faget from fusel-oil; and a third has been said by several chemists to be obtained, together with octyl alcohol, by distilling castor-oil with excess of potash; but, according to the most trustworthy experiments, there is but one alcohol obtained by this process, viz., an 8-carbon alcohol.

OCTYL ALCOHOLS AND ETHERS.

Alcohols having the composition $C_8H_{18}O$ are obtained: 1. From the octane or octyl hydride of American petroleum, by the series of processes already indicated in the case of hexyl alcohol. 2. By distilling castor-oil with potash. The first is an oily liquid, having a specific gravity of 0·826 at 16°, and boiling at 180°–184° C. (356°–363° F.). Its structure is not exactly known, but it closely resembles the alcohol obtained from castor-oil, both in its physical properties and in its reactions.

The chloride, $C_8H_{17}Cl$, obtained by the action of chlorine on octane, is also very similar in its properties to that obtained from the alcohol of castor-oil by the action of phosphorus pentachloride.

Secondary Octyl Alcohol, or Methyl-hexyl Carbinol,



This alcohol is produced by heating castor-oil with excess of solid potassium hydrate. Castor-oil contains ricinoleic acid, $C_{18}H_{34}O_3$; and this acid, when heated with potash, yields free hydrogen, a distillate containing methyl-hexyl carbinol, together with products of its decomposition, and a residue of potassium sebate:

$$\underset{\text{Ricinoleic acid.}}{C_{18}H_{34}O_3} + 2KOH = \underset{\text{Octyl alcohol.}}{C_8H_{18}O} + \underset{\text{Potassium sebate.}}{C_{10}H_{16}K_2O_4} + H_2.$$

To separate the alcohol, the distillate is repeatedly rectified over fused potash, the portion boiling below 200° C. (392° F.) only being collected: this liquid, subjected to fractional distillation, yields a portion boiling at 181°, which is the pure secondary octyl alcohol. The portions of the original distillate having a lower boiling point, consist of olefines, amongst which octylene, C_8H_{16}, boiling at 125° C. (257° F.), preponderates.*

Methyl-hexyl carbinol is a limpid oily liquid, having a strong aromatic odor, and making grease spots on paper. It has no action on polarized light. It has a specific gravity of 0·823 at 17°, and boils at 181° C. (358° F.). It is insoluble in water, but dissolves in alcohol, ether, wood-spirit, and acetic acid. It mixes with sulphuric acid, forming octyl-sulphuric acid, $C_8H_{17}HSO_4$, generally also octylene and neutral octyl-sulphate. Fused zinc chloride converts it into octylene. With potassium and sodium it yields substitution-products.

Methyl-hexyl carbinol, oxidized with potassium bichromate and sulphuric acid, yields the corresponding ketone, viz., methyl-œnanthol,

$(CO)''(C_6H_{13})(CH_3)$, or $C\begin{cases} C_6H_{13} \\ CH_3 \\ O'' \end{cases}$; thus,

$$C\begin{cases} C_6H_{13} \\ CH_3 \\ H \\ OH \end{cases} + O = OH_2 + C\begin{cases} C_6H_{13} \\ CH_3 \\ O \end{cases}$$

Methyl-hexyl carbinol. — Methyl œnanthol.

* *Schorlemmer*, Proceedings of the Royal Society, xvi. 376.

By the prolonged action of the oxidizing mixture, this ketone is further oxidized to caproic and acetic acids:

$$\underset{\text{Methyl œnanthol.}}{C_8H_{16}O} + O_4 = \underset{\text{Caproic acid.}}{C_6H_{12}O_2} + \underset{\text{Acetic acid.}}{C_2H_4O_2} + OH_2.$$

These reactions show that the alcohol produced from castor-oil is a secondary alcohol; and from further considerations, for which we must refer to Schorlemmer's paper above cited, it is inferred to contain the radical isopropyl, that is, to have one of its carbon-atoms directly combined with three others.

Octyl chloride, $C_8H_{17}Cl$, produced by the action of phosphorus pentachloride on the alcohol, has a specific gravity of 0·892 at 18° C. (64° F.), and boils at 175° C. (347° F.). Heated with alcoholic potash, it yields octene, C_8H_{16}; by alcohol and potassium acetate, it is converted into octene and octyl acetate.

Nonyl Alcohol, $C_9H_{20}O$, or **Octyl Carbinol**, $C\begin{cases} C_8H_{17} \\ H_2 \\ OH \end{cases}$, is obtained by the series of reactions above described from nonane or nonyl-hydride, which is one of the constituents of American petroleum, and likewise occurs, together with nonene, C_9H_{18}, in that portion of the liquid obtained by distilling amyl alcohol with zinc chloride, which boils between 134° and 150° C. (273° and 302° F.). Nonyl alcohol boils at about 200°. Nonyl chloride, $C_9H_{19}Cl$, has a specific gravity of 0·899 at 16° C. (60° F.), and boils at 196°.

The alcohols of the series, $C_nH_{2n+2}O$, containing from 10 to 15 carbon-atoms, are not known, but compound ethers containing 12 and 14 carbon-atoms appear to occur in spermaceti.

Sexdecyl, or **Cetyl Alcohol**, $C_{16}H_{34}O = C_{16}H_{33}(OH)$, also called *Ethal*, is obtained from spermaceti, a crystalline fatty substance found in peculiar cavities in the head of the sperm whale (*Physeter macrocephalus*). This substance consists of *cetyl palmitate*, $C_{32}H_{64}O_2$, or $C_{16}H_{31}O_2 \cdot C_{16}H_{33}$, and when heated for some time with solid potash, is resolved into potassium palmitate and cetyl alcohol:

$$C_{16}H_{31}O_2 \cdot C_{16}H_{33} + KOH = C_{16}H_{31}O_2K + C_{16}H_{33}(OH).$$

The cetyl alcohol is dissolved out from the fused mass by alcohol and ether, and purified by several crystallizations from ether.

Cetyl alcohol, or ethal, is a white crystalline mass, which melts at about 50°, and crystallizes by slow cooling in shining laminæ. It has neither taste nor smell, is insoluble in water, but dissolves in all proportions in alcohol and ether. When heated it distils without decomposition. With sodium it gives off hydrogen and yields sodium cetylate, $O_{16}H_{33}KO$. It is not dissolved by aqueous alkalies; but when heated with a mixture of potash and lime, it gives off hydrogen, and is converted into palmitic acid:

$$C_{16}H_{34}O + KOH = C_{16}H_{31}O_2K + 2H_2.$$

Distilled with phosphorus pentachloride it yields *cetyl chloride*, $C_{16}H_{33}Cl$, a limpid oily liquid, having a specific gravity of 0·8412 at 12°, and distilling with partial decomposition at a temperature above 200°. *Cetyl iodide*, $C_{16}H_{33}I$, obtained by treating the alcohol with iodine and phosphorus, is a solid substance which melts at 22°, dissolves in alcohol and ether, and crystallizes from alcohol in interlaced laminæ.

According to Heintz, cetyl alcohol, or ethal, prepared as above, is not a definite compound, but a mixture of sexdecyl alcohol, $C_{16}H_{34}O_2$, with small quantities of three other alcohols of the same series, containing re-

spectively 12, 14, and 18 atoms of carbon, inasmuch as, when fused with potash-lime, it yields the corresponding fatty acids $C_nH_{2n}O_2$.

Ceryl Alcohol, $C_{27}H_{56}O = C_{27}H_{55}(OH)$; also called *Cerotic alcohol* and *Cerotin*. — This alcohol is obtained from Chinese wax or Pela, a secretion enveloping the branches of certain trees in China, and supposed to be produced by the puncture of an insect. This wax consists mainly of *ceryl cerotate*, $C_{27}H_{53}O_2 . C_{27}H_{55}$, and is decomposed by fused potash in the same manner as spermaceti, yielding potassium cerotate and ceryl alcohol:

$$C_{27}H_{53}O_2 . C_{27}H_{55} + KOH = C_{27}H_{53}O_2K + C_{27}H_{55}(OH).$$

On digesting the fused mass with boiling water, a solution of potassium cerotate is obtained, holding ceryl alcohol in suspension; and by precipitating the cerotic acid with barium chloride and treating the resulting precipitate with alcohol, the ceryl alcohol dissolves, and may be purified by repeated crystallization from alcohol or ether. It then forms a waxy substance, melting at 97° C. (206° F.). Heated with potash-lime, it gives off hydrogen, and is converted into potassium cerotate. At very high temperatures it distils, partly undecomposed, partly resolved into water and *cerotene*, $C_{27}H_{54}$; by this character it would appear to be related to the secondary alcohols. With sulphuric acid in excess, it forms hydrated *neutral ceryl sulphate*, $(C_{27}H_{55})_2SO_4 . OH_2$.

Myricyl Alcohol, $C_{30}H_{62}O = C_{30}H_{61}(OH)$. — This alcohol, the highest known member of the series, $C_nH_{2n+2}O$, is obtained from myricin, the portion of common bees'-wax which is insoluble in boiling alcohol. Myricin consists of myricyl palmitate, $C_{16}H_{31}O_2 . C_{30}H_{62}$, and when heated with potash is decomposed in the same manner as spermaceti and Chinese wax, yielding potassium palmitate and myricyl alcohol. On dissolving the product in water, precipitating with barium chloride, exhausting the precipitate with boiling alcohol, and dissolving the substance deposited from the alcohol in mineral naphtha, pure myricyl alcohol separates as a crystalline substance, having a silky lustre. When heated, it partly sublimes unaltered, and is partly resolved (like ceryl alcohol) into water and melene, $C_{30}H_{60}$. With strong *sulphuric acid* it yields myricyl sulphate. Heated with *potash lime*, it gives off hydrogen, and is converted into potassium melissate:

$$C_{30}H_{62}O + KOH = C_{30}H_{59}O_2K + 2H_2.$$

The mother-liquor from which the myricyl alcohol has crystallized out, as above mentioned, retains a small quantity of an isomeric alcohol, which melts at 72° C. (162° F.), and when treated with potash-lime yields an acid containing a smaller proportion of carbon.

β. Monatomic Alcohols, $C_nH_{2n}O$, or $C_nH_{2n-1}OH$.

Two alcohols of this series are known, viz.:

Vinyl alcohol, $C_2H_4O = C_2H_3(OH)$.
Allyl alcohol, $C_3H_4O = C_3H_5(OH)$.

The first, discovered by Berthelot* in 1860, is produced by combining ethine or acetylene with sulphuric acid, and distilling the product with water, just as in the preparation of ethyl alcohol from ethene:

SO_4HH	+	C_2H_2	=	$SO_4H(C_2H_3)$.
Sulphuric acid.		Ethine.		Vinyl-sulphuric acid.

* Comptes Rendus, i. 805.

$$\underset{\text{Vinyl-sulphuric acid.}}{SO_4H(C_2H_3)} + \underset{\text{Water.}}{HOH} = \underset{\text{Sulphuric acid.}}{SO_4HH} + \underset{\text{Vinyl alcohol.}}{C_2H_3(OH)}$$

It is an easily decomposable liquid, having a highly pungent odor, somewhat more volatile than water, soluble in 10 to 15 parts of that liquid, and precipitated from the solution by potassium carbonate. Its chemical reactions have not been much examined, but it is probably a secondary alcohol, represented by the formula $\begin{matrix}CH_2\\ \|\\ CHOH\end{matrix}$. It is isomeric with acetic aldehyde and ethylene oxide (p. 484). The univalent radical vinyl, C_2H_3, which may be supposed to exist in it, is related to the trivalent radical ethenyl (p. 468), in the same manner as allyl to propenyl (see below).

Allyl Alcohol, C_3H_6, $= C_3H_5(OH) = \begin{matrix}CH_2\\ \|\\ CH\\ |\\ CH_2OH\end{matrix}$. — This alcohol, discovered by Cahours and Hofmann* in 1856, may be supposed to contain the univalent radical allyl, C_3H_5, derived from a saturated hydrocarbon, $\begin{matrix}CH_2\\ \|\\ CH,\\ |\\ CH_3\end{matrix}$ by abstraction of one atom of hydrogen, and isomeric with the trivalent radical propenyl, $(C_3H_2)'''$, derived in like manner from the bivalent radical propene, $\begin{matrix}-CH_2\\ |\\ -CH\\ |\\ CH_3\end{matrix}$, or from the saturated hydrocarbon propane, $\begin{matrix}CH_3\\ |\\ CH_2,\\ |\\ CH_3\end{matrix}$ by abstraction of three atoms of hydrogen. Allyl and propenyl compounds, indeed, are easily converted one into the other by addition or subtraction of two atoms of a monad element or radical.

To obtain the alcohol, allyl iodide is first prepared by the action of phosphorus tetriodide on propenyl alcohol (glycerin):

$$\underset{\text{Propenyl alcohol.}}{2(C_3H_5)'''(OH)_3} + P_2I_4 = \underset{\text{Allyl iodide.}}{2C_3H_5I} + \underset{\text{Phosphorous acid.}}{2P(OH)_3} + I_2.$$

The allyl iodide is next decomposed by silver oxalate, yielding allyl oxalate:

$$\underset{\text{Allyl iodide.}}{2C_3H_5I} + \underset{\text{Silver oxalate.}}{C_2O_4Ag_2} = \underset{\text{Silver iodide.}}{2AgI} + \underset{\text{Allyl oxalate.}}{C_2O_4(C_3H_5)_2};$$

and the allyl oxalate is decomposed by ammonia, yielding oxamide and allyl alcohol:

$$\underset{\text{Allyl oxalate.}}{C_2O_4(C_3H_5)_2} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Oxamide.}}{(C_2O_2)''(NH_2)_2} + \underset{\text{Allyl alcohol.}}{2C_3H_5(OH)}$$

* Phil. Trans., 1837, p. 1.

Allyl alcohol is a colorless liquid, having a pungent odor and a spirituous burning taste. It mixes in all proportions with water, common alcohol, and ether; boils at 103° C. (217° F.); burns with a brighter flame than common alcohol.

Allyl alcohol is a primary alcohol, similar in all its ordinary reactions to ethyl alcohol. By oxidation in contact with platinum-black, or more quickly by treatment with potassium bichromate and sulphuric acid, it is converted into acrylic aldehyde (acrolein), C_3H_5O, and acrylic acid, $C_3H_4O_2$, compounds related to it in the same manner as common aldehyde and acetic acid to ethyl alcohol. Heated with phosphoric oxide, it yields allylene, C_3H_4. With potassium and sodium it yields substitution-products. Strong sulphuric acid converts it into allyl-sulphuric acid. With the bromides and chlorides of phosphorus it yields allyl bromide, C_3H_5Br, and allyl chloride, C_3H_5Cl.

Allyl Bromides. — The monobromide, C_3H_5Br, prepared as just mentioned, or by distilling propene bromide, $C_3H_6Br_2$, with alcoholic potash, is a liquid of sp. gr. 1·47, and boiling at 62° C. (144° F.). A *tribromide of allyl*, $C_3H_5Br_3$, is obtained by adding bromine to the mono-iodide in a vessel surrounded by a freezing mixture. It is a liquid of sp. gr. 1·436 at 23° C. (73° F.), boiling at 217° C. (422° F.), and solidifying when cooled below 10° C. (50° F.). It is isomeric with propenyl bromide or tribromhydrin, obtained by the action of phosphorus pentabromide on glycerin.

A *diallyl tetrabromide*, $C_6H_{10}Br_4$, is formed by the direct combination of diallyl (p. 487) with bromine; it is a crystalline body, melting at 37°.

Allyl Iodides. — The *mono-iodide*, C_3H_5I, obtained, as above described, by distilling glycerin with phosphorus tetriodide, is a liquid of sp. gr. 1·780 at 16° C. (60° F.), and boiling at 100° C. (320° F.), It is decomposed by sodium, with formation of diallyl, C_6H_{10}. By the action of zinc or mercury and hydrochloric or dilute sulphuric acid, it is converted into propene (or allyl hydride):

$$2C_3H_5I + Zn_2 + 2HCl = ZnCl_2 + ZnI_2 + 2C_3H_6.$$

Diallyl tetriodide, $C_6H_{10}I_4$, is a crystalline body obtained by dissolving iodine in diallyl at a gentle heat.

Allyl-sulphuric Acid, $SO_4H(C_3H_5)$, is produced by adding allyl alcohol to strong sulphuric acid. The solution, diluted with water and neutralized with barium carbonate, yields barium allylsulphate, $(SO_4)_2Ba''(C_3H_5)_2$.

Allyl Oxide, $(C_3H_5)_2O$, is produced by the action of allyl iodide on potassium allylate (the gelatinous mass obtained by dissolving potassium in allyl alcohol):

$$C_3H_5OK + C_3H_5I = KI + (C_3H_5)_2O.$$

It is a colorless liquid, boiling at 82°.

Allyl Sulphide, $(C_3H_5)_2S$. — This compound exists, together with a small quantity of allyl oxide, in volatile oil of garlic, and is formed artificially by distilling allyl iodide with potassium monosulphide:

$$2C_3H_5I + K_2S = 2KI + (C_3H_5)_2S.$$

To prepare it from garlic, the sliced bulbs are distilled with water, and the crude oil thus obtained — which is a mixture of the sulphide and oxide of allyl — is subjected to the action of metallic potassium, renewed until it is no longer tarnished, whereby the allyl oxide is decomposed, after which the sulphide may be obtained pure by redistillation. In this state it forms

a colorless liquid, lighter than water, of high refractive power, possessing in a high degree the peculiar odor of the plant, and capable of being distilled without decomposition. Allyl sulphide, dissolved with alcohol and mixed with solutions of platinum, silver, and mercury, gives rise to crystalline compounds, consisting of a double sulphide of allyl and the metal, either alone or mixed with a double chloride.

Volatile oil of mustard consists of allyl sulphocyanate, C_3H_5. CNS, and will be described in connection with the sulphocyanic ethers.

Allyl Sulph-hydrate, or Allyl Mercaptan, $C_3H_5(SH)$, obtained by distilling allyl iodide with potassium sulph-hydrate, is a volatile oily liquid, having an odor like that of garlic oil, but more ethereal; boiling at 90° C. (194° F.). It attacks mercuric oxide, like ethyl mercaptan, forming the compound $(C_3H_5)_2S_2Hg''$.

γ. Monatomic Alcohols, $C_nH_{2n-2}O$, or $C_nH_{2n-3}OH$.

Only one alcohol of this series is at present known, viz.:

$$\text{Camphol, } C_{10}H_{18}O \quad = \quad C_{10}H_{17}(OH).$$

Of this compound there are several physical modifications, distinguished from one another by their action on polarized light.

One variety, called *Borneol* or *Borneo camphor*, is obtained from *Dryabalanops camphora*, being found in cavities of the trunks of old trees of that species. It has a dextro-rotatory power = 34·4°. A second, having a dextro-rotatory power of 44·9°, is produced, together with camphic acid, by the action of alcoholic potash on common camphor, to which indeed camphol bears the same relation that ethyl alcohol bears to aldehyde:

$$\underset{\text{Camphor.}}{2C_{10}H_{16}O} + OH_2 = \underset{\text{Camphol.}}{C_{10}H_{18}O} + \underset{\text{Camphic acid.}}{C_{10}H_{16}O_2}$$

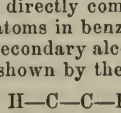
A third variety, possessing a dextro-rotatory power of 4·5°, is obtained by distilling amber with potash; and a fourth, called *lævo-camphol*, which has a lævo-rotatory power of 33·4° (equal and opposite to that of borneol), is found in the alcohol produced in the fermentation of sugar from madder-root.

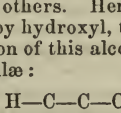
Dextro-rotatory camphol, both natural and artificial, forms small transparent, colorless crystals, apparently having the form of regular hexagonal prisms, insoluble in water, very soluble in alcohol and ether. It melts at 198° C. (388° F.), and boils at 212° C. (414° F.), distilling without alteration. Lævo-rotatory camphol forms crystalline laminæ, or a white powder, sparingly soluble in water, easily in acetic acid, alcohol, and ether. Both varieties smell like pepper and common camphor.

Camphol, distilled with phosphoric oxide, gives up water, and yields a hydrocarbon, $C_{10}H_{16}$, isomeric with turpentine oil. When boiled with nitric acid, it gives off two atoms of hydrogen, and is reduced to the corresponding aldehyde, viz., common or laurel camphor, $C_{10}H_{16}O$, which is dextro- or lævo-rotatory, according to the variety of camphol used. With other acids, camphol behaves like alcohols in general, forming ethers: thus, when heated in a sealed tube with strong hydrochloric acid, it forms *camphor chloride*, $C_{10}H_{17}Cl$, a crystalline lævo-rotatory substance isomeric with hydrochloride of turpentine oil, $C_{10}H_{16}$. HCl (p. 489). With benzoic acid camphol forms *camphyl benzoate*, $C_7H_5O_2$. $C_{10}H_{17}$.

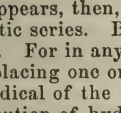
δ, Monatomic Alcohols, $C_nH_{2n-6}O$, or $C_nH_{2n-7}OH$.

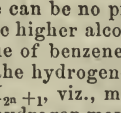
These alcohols correspond to the aromatic hydrocarbons, and are therefore called *aromatic alcohols*. The lowest member of the series corresponds to benzene, and therefore contains six atoms of carbon. Now, the constitutional formula of benzene (p. 493) shows that in this hydrocarbon every carbon-atom is directly combined with two others. Hence, when one of the hydrogen-atoms in benzene is replaced by hydroxyl, the resulting alcohol must be a secondary alcohol. The relation of this alcohol, called *phenol*, to benzene, is shown by the following formulæ:

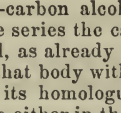

Benzene.


Phenol.

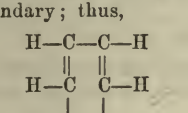
It appears, then, that there can be no primary six-carbon alcohol of the aromatic series. But with the higher alcohols of the series the case is different. For in any homologue of benzene, —formed, as already observed, by replacing one or more of the hydrogen-atoms in that body with an alcohol radical of the series C_nH_{2n+1}, viz., methyl and its homologues, —the substitution of hydroxyl for hydrogen may take place either in the benzene molecule itself, or in the methyl, ethyl, &c., attached to it; in the latter case the carbon-atom united with hydroxyl will be directly combined with only one other atom of carbon, so that a primary alcohol will result; but in the former case, the carbon united with hydroxyl will still be combined also with two other atoms of carbon, so that the resulting alcohol will be secondary; thus,

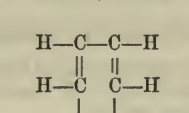

Methyl benzene, or Toluene.

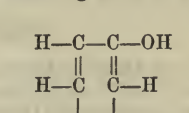

Primary alcohol.

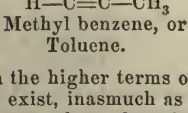

Secondary alcohol.

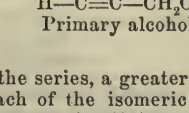
In the higher terms of the series, a greater number of isomeric alcohols may exist, inasmuch as each of the isomeric hydrocarbons containing a given number of carbon-atoms (p. 494) may furnish a primary and a secondary monatomic alcohol. Thus the formulæ C_8H_{10} include sethyl benzene, $C_6H_5(C_2H_5)$, and dimethyl benzene, $C_6H_4(CH_3)_2$, to each of which there corresponds a primary and a secondary alcohol:

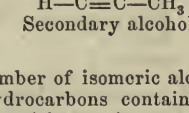

Ethyl-benzene.


Primary alcohol.


Secondary alcohol.


Dimethyl-benzene.


Primary alcohol.


Secondary alcohol.

The constitution of the primary aromatic alcohols is similar to that of the alcohols of the methyl series, in this respect, that the carbon-atom combined with hydroxyl is also directly associated with two atoms of hydrogen; and accordingly these alcohols, when subjected to the action of oxidizing agents, easily give up these two atoms of hydrogen in exchange for an atom of oxygen, and are thereby converted into acids, the group, CH_2OH, being converted into COOH, just as in the conversion of common alcohol, CH_3CH_2OH, into acetic acid, CH_3COOH. But in the secondary aromatic alcohols, or phenols, the carbon-atom united with hydroxyl, has its three other units of equivalence satisfied by combination with two other carbon-atoms, and there is no hydrogen in its immediate neighborhood to be exchanged for oxygen: hence, these alcohols are not converted by oxidation into acids containing the same number of carbon-atoms.

The actually known alcohols of the aromatic series are the following:

Primary.		*Secondary.*	
		Phenol,	C_6H_5OH
Benzyl alcohol,	$C_6H_5.CH_2OH$	Cresol,	$C_6H_4(CH_3)OH$
		Phlorol,	$C_6H_4(C_2H_5)OH$
Xylyl alcohol,	$C_7H_7.CH_2OH$	Dimethyl phenol,	$C_6H_3(CH_3)_2OH$
Cymyl alcohol,	$C_9H_{11}.CH_2OH$	Thymol,	$C_6H_3(C_2H_5)_2OH$?
Sycoceryl alcohol,	$C_{17}H_{27}.CH_2OH$		

The secondary aromatic alcohols are often designated by the generic name of *phenols;* thus cresol is methyl-phenol, phlorol is ethyl-phenol, &c. There are also diatomic and triatomic phenols, which will be noticed hereafter.

PRIMARY AROMATIC ALCOHOLS.

Benzyl Alcohol, $C_7H_8O=C_7H_7(OH)=C_6H_5.CH_2OH$; also called *Benzoic alcohol.**—This alcohol is produced: 1. By the action of alcoholic potash on benzoic aldehyde (bitter-almond oil):

$2C_7H_6O$	+	KOH	=	C_7H_8O	+	$C_7H_5O_2K$
Benzoic aldehyde.				Benzyl alcohol.		Potassium benzoate.

2. From toluene, C_7H_8, by converting that compound into benzyl chloride, C_7H_7Cl, by the action of chlorine at high temperatures (p. 496), and distilling this chloride with potash:

$$C_7H_7Cl + KOH = KCl + C_7H_7OH.$$

3. Together with other products, by the action of nascent hydrogen on benzoic or hippuric acid (see those acids).

Benzyl alcohol is a colorless, strongly refracting, oily liquid, having a specific gravity of 1·051 at 14° C. (57° F.), and boiling at 206·5° C. (404° F.). It is insoluble in water, but soluble in all proportions in common alcohol, ether, acetic acid, and carbon bisulphide. By oxygen in presence of platinum black, or by nitric acid, it is converted into benzoic aldehyde; by aqueous chromic acid, into *benzoic acid:*

$C_6H_5.CH_2OH$	+	O	=	OH_2	+	$C_6H_5.COH$
Benzyl alcohol.						Benzoic aldehyde.
$C_6H_5.CH_2OH$	+	O_2	=	OH_2	+	$C_6H_5.CO(OH)$
Benzyl alcohol.						Benzoic acid.

* *Cannizzaro,* Ann. Ch. Pharm. lxxxviii. 129; xc. 252; xcii. 113.

Heated with boric oxide, it is converted into *benzyl oxide*, $C_7H_7OC_7H_7$, or $(C_7H_7)_2O$:

$$2C_7H_7(OH) - OH_2 = (C_7H_7)_2O.$$

Strong hydrochloric acid converts it into *benzyl chloride*, C_7H_7Cl (p. 496). Distilled with acetic acid and strong sulphuric acid, it is converted into *benzyl acetate*, $C_7H_7(OC_2H_3O)$, a liquid having an odor of pears, and boiling at 210° C. (410 F.)

Xylyl Alcohol, $C_8H_{10}O = C_8H_9(OH) = C_7H_7.CH_2OH$, or $C_6H_4(CH)_3.CH_2OH$, also called *Toluylic alcohol.* — The formation of this compound is exactly analogous to that of the preceding, viz.: 1. Together with toluic acid, $(C_8H_8O_2)$, by the action of alcoholic potash on toluic aldehyde, (C_8H_8O). 2. By distilling xylyl chloride (p. 498) with potash. It is a white crystalline body, which melts between 58·5° and 59·5° C. (138° and 140° F.), and boils at 217° C. (422° F.). Nitric acid converts it into toluic aldehyde.

Xylyl chloride, C_9H_9Cl, is obtained, as already observed, by the action of chlorine on xylene-vapor at high temperatures; and this chloride, treated with sulph-hydrate and potassium sulphide, yields *xylyl sulph-hydrate*, $C_8H_9(SH)$, and *xylyl sulphide* $(C_8H_9)_2S$.

Cymyl Alcohol, $C_{10}H_{14}O = C_{10}H_{13}(OH) = C_9H_{11}.CH_2OH$, also called *Cumylic Alcohol.*—This alcohol, discovered by Kraut,* is produced by the action of alcoholic potash on cuminic aldehyde:

$2C_{10}H_{12}O$	+	KOH	=	$C_{10}H_{11}O_2K$	+	$C_{10}H_{14}O$
Cuminic aldehyde.				Potassium cuminate.		Cymyl alcohol.

It is a colorless liquid, boiling at 243° C. (470° F.), insoluble in water, soluble in all proportions in common alcohol and ether. Nitric acid converts it into *cuminic acid.* Boiled with alcoholic potash, it is converted into *potassium cuminate* and *cymene:*

$3C_{10}H_{14}O$	+	KOH	=	$C_{10}H_{11}O_2K$	+	$2C_{10}H_{14}$	+	$2OH_2$
Cymyl alcohol.				Potassium cuminate.		Cymene.		

Hydrochloric acid gas converts it into *cymyl chloride*, $C_{10}H_{13}Cl$.

Sycoceryl Alcohol, $C_{18}H_{30}O = C_{18}H_{29}(OH) = CH_{17}H_{27}.CH_2OH$.—This compound, discovered by De la Rue and Müller,† is produced by the action of alcoholic soda on sycoceryl acetate (a crystalline substance extracted from the resin of *Ficus rubiginosa*), and purified by precipitation with water or by crystallization from common alcohol. It forms very thin crystals resembling caffeine, and melting at 90° to a liquid heavier than water. It is slowly attacked by dilute nitric acid, yielding a crystalline mass apparently consisting of a mixture of *sycoceric acid*, $C_{18}H_{28}O_2$, and *nitrosycoceric acid*, $C_{18}H_{27}(NO_2)O_2$. Boiled with dilute aqueous chromic acid, it yields thin prisms, probably of *Sycoceric aldehyde*, $C_{18}H_{28}O$. With acetyl chloride, it forms crystalline *sycoceryl acetate:*

$C_{18}H_{29}OH$	+	C_2H_3OCl	=	HCl	+	$C_{18}H_{29}OC_2H_3O$
Sycoceryl alcohol.		Acetyl chloride.				Sycoceryl acetate.

With benzoic acid it yields, in like manner, *sycoceryl benzoate*, $C_{18}H_{29}OC_7H_5O$, which crystallizes in prisms from solution in benzene or chloroform.

The resin of *Ficus rubiginosa*, an Australian plant, is resolved by treatment with alcohol, into about 73 per cent. of *sycoretin*, soluble in cold alcohol,

* Ann. Ch. Pharm. xcii. 66. † Phil. Trans. 1860, p. 43.

14 per cent. of sycoceryl acetate, soluble in hot alcohol, and 13 per cent. of residue, consisting of caoutchouc, sand, and fragments of bark. *Sycoretin* is an amorphous white neutral resin, very brittle and highly electric; it melts in boiling water to a thick liquid which floats on the surface. It dissolves easily in alcohol, ether, chloroform, and oil of turpentine.

SECONDARY AROMATIC ALCOHOLS; PHENOLS.

Phenol, $C_6H_6O = C_6H_5OH$.—*Phenyl alcohol, Phenic acid, Carbolic acid, Coal-tar creosote.*—This compound is produced: 1. By the action of nitrous acid on aniline (amidobenzene):

$$\underset{\text{Aniline.}}{C_6H_5(NH_2)} + \underset{\substack{\text{Nitrous}\\\text{acid.}}}{NO(OH)} = \underset{\text{Phenol.}}{C_6H_5(OH)} + OH_2 + N_2$$

2. By the dry distillation of salicylic acid:

$$\underset{\substack{\text{Salicylic}\\\text{acid.}}}{C_7H_6O_3} = \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Phenol.}}{C_6H_6O}$$

It may be conveniently prepared by heating crystallized salicylic acid strongly and quickly in a glass retort, either alone or mixed with pounded glass or quicklime. Phenol then passes over into the receiver, and crystallizes almost to the last drop.

3. Phenol is produced in the dry distillation of coal, and forms the chief constituent of the acid portion of coal-tar oil; this is the source from which it is most frequently obtained. Crude coal-tar oil is agitated with a mixture of slaked lime and water, the whole being left for a considerable time; the aqueous liquid is then separated from the undissolved oil, decomposed by hydrochloric acid, and the oily product thus obtained is purified by cautious distillation, the first third only being collected. Or the coal-tar oil is subjected to distillation in a retort furnished with a thermometer, and the portion which passes over between the temperatures of 150° and 200° C. (302° and 390° F.) is collected apart. This product is then mixed with a hot, strong solution of caustic potash, and left to stand, whereby a whitish, somewhat crystalline, pasty mass is obtained, which by the action of water is resolved into a light oily liquid and a dense alkaline solution. The latter is withdrawn by a siphon, decomposed by hydrochloric acid, and the separated oil purified by contact with calcium chloride, and redistillation. Lastly, it is exposed to a low temperature, and the crystals formed are drained from the mother-liquid and carefully preserved from the air.

Pure phenol forms long, colorless, prismatic needles, which melt at 35° C. (95° F.) to an oily liquid, boiling at 180° C. (356° F.), and greatly resembling creosote* in many particulars, having a very penetrating odor and burning taste, and attacking the skin of the lips. Its sp. gr. is 1·065. It is slightly soluble in water, freely in alcohol and ether, and has no acid reaction to test-paper. The crystals absorb moisture with avidity, and liquefy.† It coagulates albumen, and is a powerful antiseptic, preserving meat and other animal substances from decomposition, and even removing the fetid odor from them after they have begun to putrefy. It has also

* A considerable portion of the creosote of commerce consists of phenol or carbolic acid, more or less pure.

† Phenol prepared from salicylic acid is much less deliquescent than that obtained from coal-tar.

been successfully used by Mr. Crookes for destroying the infection of cattle plague. Sulphur and iodine dissolve in it; nitric acid, chlorine, and bromine attack it with energy, forming substitution-products, all of which are of acid character: thus with chlorine it forms the two compounds, $C_6H_4Cl_2O$ and $C_6H_3Cl_3O$; and with nitric acid the three products, $C_6H_5(NO_2)O$, $C_6H_4(NO_2)_2O$, and $C_6H_3(NO_2)_3O$.

With sulphuric acid, phenol forms *sulphophenic acid*, $C_6H_6SO_4$, or $C_6H_5OSO_3H$, which assumes a syrupy state in a dry vacuum. This acid is to a certain extent analogous in composition to ethylsulphuric acid, and forms a soluble barium salt, which crystallizes from alcohol in minute needles.

Phenol dissolves in alkalies, forming salts called *phenates*, which, however, are difficult to obtain in definite form. *Potassium phenate*, C_6H_5KO, obtained by heating phenol with potassium, or with solid potassium hydrate, crystallizes in fine white needles. On heating this potassium-compound with iodide of methyl, ethyl, or amyl, double ethers are produced, viz., methyl-phenate, or anisol, $C_6H_5OCH_3$; ethyl-phenate, or phenetol, $C_6H_5OC_2H_5$, and amyl-phenate, or phenamylol, $C_6H_5OC_5H_{11}$. These bodies resemble the mixed ethers of the ordinary alcohols (p. 509) in composition and mode of formation, but differ greatly from them in their behavior with sulphuric and nitric acids, with which in fact they behave just like phenol itself, forming substitution-products possessing acid properties.

Methyl phenate, or *Anisol*, $C_7H_8O = C_6H_5OCH_3$, is also produced, with evolution of carbon dioxide, by the dry distillation of methyl salicylate, $C_7H_5O_3 . CH_3$, just as phenol is obtained from salicylic acid or hydrogen salicylate, $C_7H_5O . H$:

$C_7H_5O_3 . CH_3$	=	CO_2	+	$C_6H_5O . CH_3$
Methyl salicylate.				Methyl phenate.

In the same manner also may ethyl phenate and amyl phenate be obtained from the corresponding ethers of salicylic acid.

Anisol is a colorless, very mobile liquid, having a pleasant aromatic odor, a specific gravity of 0·991 at 15° C. (59° F.), and boiling without decomposition at 152° C. (306° F.). It dissolves completely in strong sulphuric acid, forming *sulphanisolic acid*, $C_7H_8SO_4$. Fuming nitric acid acts strongly on anisol, forming three substitution-products, each of which when treated with a reducing agent, such as ammonium sulphide, yields a corresponding basic amido-compound: thus,

$C_7H_7(NO_2)O$ Nitranisol.	$C_7H_7(NH_2)O$ Nitranisidine.
$C_7H_6(NO_2)_2O$ Dinitranisol.	$C_7H_6(NH_2)_2O$ Dinitranisidine.
$C_7H_5(NO_2)_3O$ Trinitranisol.	$C_7H_5(NH_2)_3O$ Trinitranisidine.

No such substitution-products are obtained from the mixed or compound ethers of any primary alcohol.

Phenol, distilled with *phosphorus pentachloride*, yields a distillate containing a small quantity of phenyl chloride or chloro-benzene, C_6H_5Cl (p. 494), and a residue containing a triphenyl phosphate, $PO_4(C_6H_5)_3$, or diphenyl phosphate, $PO_4(C_6H_5)_2H$; but the conditions under which one or the other of these compounds is formed have not been exactly determined.

With *benzoic chloride*, phenol yields a white, fusible crystalline compound consisting of phenyl benzoate, or benzyl phenol:

$C_6H_5(OH)$	+	C_7H_5OCl	=	HCl	+	$C_6H_5OC_7H_5O$
Phenol.		Benzoic chloride.				Phenyl benzoate.

Phenol, heated for a long time with *ammonia* in sealed tubes, is converted into aniline, C_6H_7N.

Chlorophenols.—Monochlorophenol has not been obtained.

Dichlorophenol, or *Chlorophenesic acid*, $C_6H_4Cl_2O$, is produced by the comparatively feeble action of chlorine on phenol, but is best obtained by the dry distillation of dichlorosalicylic acid. It is a volatile oil, insoluble in water, easily soluble in alcohol or ether.

Trichlorophenol, or *Chlorophenisic acid*, $C_6H_3Cl_3O$, is the principal product of the action of chlorine on phenol. It may be conveniently prepared from those portions of crude coal-oil which boil between 182° and 204° C. (360° and 400° F.). The oil is saturated with chlorine, and distilled in the open air, the first and last portions being rejected; and the product is again treated with chlorine until the whole solidifies. The crystals are drained and dissolved in hot dilute solution of ammonia: on cooling, the sparingly soluble ammonium chlorophenisate crystallizes out. This is dissolved in pure water, decomposed by hydrochloric acid, washed, and lastly distilled.

Chlorophenisic acid forms exceedingly fine, colorless, silky needles, which melt when gently heated: it has a very penetrating, persistent, and characteristic odor, is very sparingly soluble in water, but dissolves freely in alcohol, ether, and hot concentrated sulphuric acid. It slowly sublimes at common temperatures, and distils with ebullition when strongly heated. It forms well-defined salts, the general formula of which is $C_6H_2MCl_3O$. When treated in alcoholic solution with excess of chlorine, it is converted into pentachlorophenol, or chlorophenusic acid, C_6HCl_5O, which is also crystalline.

Bromophenols.—Three bromophenols have been obtained, viz., C_6H_5BrO and $C_6H_4Br_2O$, by distillation of monobromosalicylic and dibromosalicylic acids; and $C_6H_3Br_3O$ by the action of bromine in excess on phenol. The first is liquid; the other two are crystalline.

Iodophenols, C_6H_5IO, $C_6H_4I_2O$, and $C_6H_3I_3O$, are produced by the action of iodine-chloride on phenol.

Nitrophenols.—Three of these compounds are known, all of acid character.

Mononitrophenol, or *Nitrophenasic acid*, $C_6H_5(NO_2)O$, is obtained by distilling phenol with very dilute nitric acid, in beautiful yellow needles, soluble in ammonia and potash, and yielding a beautiful red silver salt, $C_6H_4Ag(NO_2)O$.

Dinitrophenol, or *Nitrophenesic acid*, $C_6H_4(NO_2)_2O$, may be prepared directly from the oil which is employed in the preparation of mononitrophenol. The oil is carefully mixed in a large open vessel with rather more than its own weight of ordinary nitric acid. The action is very violent. The brownish-red substance produced is slightly washed with water, then boiled with dilute ammonia, and filtered hot. A brown mass remains on the filter, which is preserved to prepare trinitrophenol, and the solution deposits on cooling a very impure ammoniacal salt of nitrophenesic acid, which requires several successive crystallizations, after which it is decomposed by nitric acid, and the product is crystallized from alcohol.

Nitrophenesic acid forms yellow prismatic crystals, very sparingly soluble even in boiling water, but freely soluble in alcohol. It has no odor. Its taste, at first feeble, becomes after a short time very bitter. It melts at 104°, and crystallizes on cooling. In very small quantity it may be distilled without decomposition, but when briskly heated it often detonates, but not violently. The salts of this acid are yellow or orange, and very beautiful; they are mostly soluble in water, and detonate feebly when heated.

Trinitrophenol, or *Nitrophenisic acid*— generally called *Picric acid*, and sometimes *Carbazotic acid* — $C_6H_3N_3O_7 = C_6H_3(NO_2)_3O$. — This acid may be economically prepared from impure nitrophenesic acid, or from the brown mass insoluble in dilute ammonia already referred to. It is purified by a process similar to that employed in the case of the preceding compound.

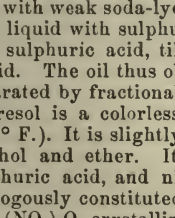
It is also one of the ultimate products of the action of nitric acid upon indigo and numerous other substances, as silk, wool, several resins, especially that of *Xanthorræa hastilis* (yellow gum of Botany Bay), salicin and some of its derivatives, coumarin, &c. It may be prepared from indigo by adding that substance in coarse powder, and by small proportions, to 10 or 12 times its weight of boiling nitric acid of sp. gr. 1·43. When the last of the indigo has been added, and the action, at first extremely violent, has become moderate, an additional quantity of nitric acid may be poured upon the mixture, and the boiling kept up until the evolution of red fumes nearly ceases. When cold, the impure picric acid obtained may be removed, converted into potassium-salt, several times recrystallized, and lastly, decomposed by nitric acid. In the pure state it forms beautiful pale-yellow scaly crystals, but slightly soluble in cold water and of insupportably bitter taste. Picric acid is now extensively used in dyeing yellow. It forms a series of crystallizable salts of a yellow or orange color. The potassium salt, $C_6H_2K(NO_2)_3O$, forms brilliant needles, and is so little soluble in cold water that a solution of picric acid is occasionally used as a precipitant for potassium. The alkaline salts of this acid explode by heat with extraordinary violence.

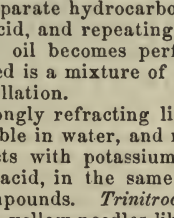
When a solution of picric acid is distilled with calcium hypochlorite, or a mixture of potassium chlorate and hydrochloric acid, an oily liquid of a penetrating odor is obtained, having a sp. gr. of 1·665, and boiling between 114° and 115° C. (237° and 239° F.). This substance, *chloropicrin*, has the composition CNO_2Cl_3, which is that of chloroform ($CHCl_3$), having the hydrogen replaced by nitryl. *Bromopicrin*, CNO_2Br_3, is obtained in like manner by treating picric acid with calcium hypobromite.

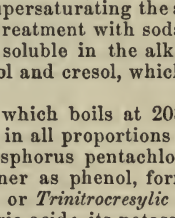
Cresol, $C_7H_8O = C_6H_4(CH_3) . OH$. — This compound exists, together with phenol, in the so-called coal-tar creosote, and is separated by fractional distillation. It is also contained, together with phenol and other compounds, in the tar of pine-wood, and is obtained therefrom by treating the oil which passes over in distillation between 150° and 220° C. (302° and 408° F.), with weak soda-lye to separate hydrocarbons, supersaturating the alkaline liquid with sulphuric acid, and repeating the treatment with soda-lye and sulphuric acid, till the oil becomes perfectly soluble in the alkaline liquid. The oil thus obtained is a mixture of phenol and cresol, which are separated by fractional distillation.

Cresol is a colorless, strongly refracting liquid, which boils at 203° C. (397° F.). It is slightly soluble in water, and mixes in all proportions with alcohol and ether. It reacts with potassium, phosphorus pentachloride, sulphuric acid, and nitric acid, in the same manner as phenol, forming analogously constituted compounds. *Trinitrocresol*, or *Trinitrocresylic acid*, $C_7H_5(NO_2)_3O$, crystallizes in yellow needles like picric acid: its potassium-salt, $C_7H_4K(NO_2)_3O$, in orange-red needles, moderately soluble in water.

Crysol is isomeric with benzyl alcohol and with anisol: the difference of constitution of these three compounds is exhibited in the following diagrams:


Benzyl alcohol.


Cresol.


Anisol.

Eight-carbon Xylylic Phenols, $C_8H_{10}O$. — This formula may include two secondary alcohols, isomeric with xylyl alcohol, viz.,

Dimethyl-phenol	$C_6H_3(CH_3)_2OH$
Ethyl-phenol	$C_6H_4(C_2H_5)OH$.

A xylylic phenol is mentioned by Hugo Müller* as occurring in coal-tar. This is probably dimethyl phenol, inasmuch as products obtained by destructive distillation have hitherto been found to contain only methyl derivatives of benzene. The portion of aloïsol (a product obtained by distilling aloes with lime), which is soluble in potash, has, according to Rembold,† the composition of a xylylic phenol, and is, perhaps, identical with that occurring in coal-tar.

Phlorol, an oily liquid obtained by the dry distillation of the barium salt of phloretic acid, $C_9H_{10}O_3$, has also the composition $C_8H_{10}O$, and probably consists of ethyl-phenol. Its formation is represented by the equation,

$$C_9H_{10}O_3 = CO_2 + C_8H_{10}O.$$

Phlorol is a colorless, strongly refracting oil, having a specific gravity of 1·0374 at 12° C. (54° F.), and boiling between 190° and 200°. It dissolves in strong sulphuric acid, forming a sulpho-acid which yields a soluble barium salt. With *chlorine* it forms a substitution-product. It reacts violently with strong nitric acid, forming the compound, $C_8H_7(NO_2)_3O$.

Ten-carbon Phenols.—The formula, $C_{10}H_{14}O$, may evidently include a considerable number of phenols isomeric with cymyl alcohol (p. 549); only one of these, however, is known, viz., *thymol*, and even of this the exact constitution has not been ascertained.

Thymol, $C_{10}H_{14}O$, is a crystalline body, occurring (together with thymene, $C_{10}H_{16}$, and cymene, $C_{10}H_{14}$) in the volatile oil of thyme (*Thymus vulgaris*). It sometimes crystallizes out spontaneously, and may in all cases be separated by agitating the oil with soda-solution, and supersaturating the alkaline liquid with hydrochloric acid. It is also obtained from the volatile oil of horse-mint (*Monarda punctata*), and from that of an East Indian umbelliferous plant called *Ptychotis Ajowan*.

Thymol crystallizes in transparent rhomboïdal plates, melting at 44°. It has a mild odor, peppery taste, and boils without decomposition at 220° C. (428° F.). It is distinguished from cymyl alcohol by yielding with oxidizing agents, not cuminic acid, but thymoïl, $C_{12}H_{16}O_2$. With sodium it forms the compound, $C_{10}H_{13}NaO$, which absorbs carbon dioxide, forming the sodium salt of thymotic acid, $C_{10}H_{14}O_3$, or $C_{10}H_{14}O.CO_2$. Strong *sulphuric acid* converts thymol into *thymylsulphuric acid*, $C_{10}H_{14}SO_4$. With *bromine* in sunshine it yields *pentabromothymol*, $C_{10}H_9Br_5O$; and with *chlorine*, $C_{10}H_{11}Cl_3O$, or $C_{10}H_9Cl_5O$, according as the reaction takes place in the shade or in sunshine; both these, as well as the bromine-compound, are crystalline.

There are two *nitro-thymols*, $C_{10}H_{12}(NO_2)_2O$ and $C_{10}H_{11}(NO_2)_3O$, obtained by the action of nitric acid on thymyl-sulphuric acid. Both form potassium-salts, which crystallize in yellow or orange-yellow needles.

ε. Monatomic Alcohols, $C_nH_{2n-8}O$, or $C_nH_{2n-7}(OH)$.

Two only of these bodies are known, viz., cinnyl alcohol and cholesterin.

Cinnyl Alcohol, Styryl Alcohol, or Styrone, $C_9H_{10}O$, or C_9H_9OH, is obtained by heating styracin or cinnyl cinnamate, $C_9H_9(OC_9H_7O)$, (a compound contained in liquid storax and in balsam of Peru,) with caustic alkalies. It crystallizes in soft silky needles, having a sweet taste and an odor of hyacinths, melting at 33°, and volatilizing, without decomposition, at a higher

* Zeitschrift für Chemie, 1865, p. 271. † Ann. Ch. Pharm. cxxxviii. 186.

temperature. It is moderately soluble in water, freely in alcohol and ether. By oxidizing agents it is converted into *cinnamic aldehyde*, C_9H_8O, and *cinnamic acid*, $C_9H_8O_2$, being related to those compounds in the same manner as ethyl alcohol to acetic aldehyde and acetic acid. With *fuming sulphuric acid* it forms a sulpho-acid, $C_9H_{10}SO_3$, the barium-salt of which is soluble in water.

Cholesterin, $C_{26}H_{44}O = C_{26}H_{43}(OH)$. — This substance is found in small quantity in various parts of the animal system, as in the bile, the brain and nerves, and the blood: it forms the chief ingredient of *biliary calculi*, from which it is easily extracted by boiling the powdered gall-stones in strong alcohol, and filtering the solution while hot; on cooling, the cholesterin crystallizes in brilliant colorless plates. It is a fatty substance, insoluble in water, tasteless and inodorous; it is freely soluble in boiling spirit and in ether, and crystallizes from the alcoholic solution in beautiful white laminæ having a mother-of-pearl lustre. It melts at 137° C. (279° F.), and sublimes at 200° C. (392° F.).

Heated with strong sulphuric acid, it gives up water, and yields a resinous hydrocarbon, $C_{26}H_{42}$. With nitric acid it yields cholesteric acid, $C_8H_{10}O_5$, together with other products. With chlorine and bromine it forms substitution-products. Heated to 200° with acetic, butyric, benzoic, and stearic acids, it forms compound ethers, thus:

$C_{26}H_{43}(OH)$	+	$C_{18}H_{35}O(OH)$	=	$C_{26}H_{43}(OC_{18}H_{35}O)$	+	OH_2
Cholesterin.		Stearic acid.		Cholesteryl stearate.		

DIATOMIC ALCOHOLS AND ETHERS.

The diatomic alcohols are derived from saturated hydrocarbons by substitution of two equivalents of hydroxyl for two atoms of hydrogen, and may, therefore, be regarded as compounds of bivalent alcohol radicals with two equivalents of hydroxyl. Thus ethene alcohol, $C_2H_6O_2$, may be formulated in either of the three following ways:

$$C\begin{cases} CH_3 \\ H \\ OH \\ OH \end{cases} \qquad \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} \qquad (C_2H_4)''(OH)_2;$$

the first of which represents it as a derivative of methane, CH_4; the second as a derivative of ethane $\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix}$; the third as a compound of ethene, C_2H_4, with hydroxyl; or as derived from a double molecule of water, $H_2(OH)_2$, by substitution of ethene for two atoms of hydrogen.

Two series of these alcohols are known; the first derived from the paraffins, the second from the aromatic hydrocarbons.

1.—Diatomic Alcohols, $C_nH_{2n+2}O_2$, or $(C_nH_{2n})''(OH)_2$.

The alcohols of this series are designated by the generic name of *glycols*.* They may be regarded as compounds of olefines with two equivalents of hydroxyl. The following are known:

* This term, formed from the first syllable of *glycerin* and the last of *alcohol*, indicates that the compounds to which it is applied are intermediate between the alcohols, commonly so called, and the glycerins or triatomic alcohols.

Name.	Formula.	Boiling point.
Ethene alcohol . . .	$C_2H_6O_2 = C_2H_4(OH)_2$	197·5° C. (388° F.).
Propene alcohol . .	$C_3H_8O_2 = C_3H_6(OH)_2$	188°–189° C. (370°–372° F.).
Quartene or Butylene alcohol . .	$C_4H_{10}O_2 = C_4H_8(OH)_2$	183°–184° C. (361°–365° F.).
Quintene or Amylene alcohol . .	$C_5H_{12}O_2 = C_5H_{10}(OH)_2$	177° C. (351° F.).
Octene alcohol . . .	$C_8H_{18}O_2 = C_8H_{16}(OH)_2$	235°–240° C. (455°–464° F.).

Methene alcohol, $CH_2(OH)_2$, has not been obtained.

The glycols are formed by the following processes:

1. By combining an olefine with bromine; treating the resulting dibromide with an alcoholic solution of potassium acetate or with silver acetate, whereby it is converted into a diacetate of the olefine; and decomposing this compound with solid potassium hydrate, whereby potassium acetate and a diatomic alcohol are formed, the latter of which may be distilled off.

$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + 2AgOC_2H_3O = 2AgBr + \begin{matrix} CH_2OC_2H_3O \\ | \\ CH_2OC_2H_3O \end{matrix}$$

Ethene bromide. Silver acetate. Ethene diacetate.

$$\begin{matrix} CH_2OC_2H_3O \\ | \\ CH_2OC_2H_3O \end{matrix} + 2KOH = 2KOC_2H_3O + \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

Ethene diacetate. Potassium hydrate. Potassium acetate. Ethene alcohol.

2. By treating a monochlorohydrate corresponding to a triatomic alcohol (a glycerin) with nascent hydrogen (evolved from water by sodium amalgam); the chlorine is then replaced by hydrogen, and a diatomic alcohol results; thus,

$$(C_3H_5)'''(OH)_2Cl + HH = HCl + (C_3H_6)'(OH)_2$$

Propenyl monochlorohydrate. Propene alcohol.

Properties.—The glycols are colorless, inodorous, more or less viscid liquids, freely soluble in water and alcohol; ethene alcohol is but sparingly soluble in ether; the rest dissolves easily in that liquid. The boiling points of ethene, propene, quartene, and quintene glycols, exhibit the singular anomaly of becoming lower as the molecular weight of the compound increases (see table, above): octene glycol, however, exhibits a higher boiling point. This anomaly probably arises from difference of constitution in the successive terms of the series at present known, ethene glycol being a primary alcohol, whereas the higher numbers may be secondary or tertiary alcohols. Thus the ethene and propene glycols probably differ in constitution in the manner shown by the following formulæ:

$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

Ethene alcohol.

$$\begin{matrix} H_3C & CH_3 \\ & \diagdown\diagup \\ & HOCOH \end{matrix}$$

Propene alcohol.

The reactions of the higher glycols are not sufficiently known to decide this question: it is known, however, that propene alcohol heated with hydriodic acid, yields isopropyl iodide.

The chemical reactions of the glycols have been studied chiefly in the case of ethene alcohol. They are, for the most part, similar to those of the

monatomic alcohols; but inasmuch as the glycols contain two atoms of replaceable hydrogen, or of hydroxyl, the reactions generally take place by two stages, yielding two series of products.

1. Ethene alcohol treated with *nitric acid* gives up 2 or 4 atoms of hydrogen in exchange for oxygen, and is converted into *glycollic*, or *oxalic acid*, according as the action takes place at ordinary or at higher temperatures,

$$\underset{\text{Glycol.}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} + O_2 = OH_2 + \underset{\substack{\text{Glycollic}\\\text{acid.}}}{\begin{matrix}CH_2OH\\|\\CO(OH)\end{matrix}}$$

$$\underset{\substack{\text{Ethene}\\\text{alcohol.}}}{\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}} + O_4 = 2OH_2 + \underset{\text{Oxalic acid.}}{\begin{matrix}CO(OH)\\|\\CO(OH)\end{matrix}}$$

Under certain circumstances the corresponding aldehydes are also produced, as *glyoxal*, $\begin{matrix}COH\\|\\COH\end{matrix}$, from ethene alcohol, by removal of four hydrogen-atoms without substitution.

Ethene alcohol is also converted into oxalic acid by fusion with *potash:*

$$\underset{\substack{\text{Ethene}\\\text{alcohol.}}}{C_2H_6O_2} + 2KOH = \underset{\substack{\text{Potassium}\\\text{oxalate.}}}{C_2O_4K_2} + 4H_2$$

Propene glycol, $C_3H_6O_2$, is converted into *lactic acid*, $C_3H_6O_3$, by slow oxidation in contact with platinum black. When heated with dilute nitric acid it yields *glycollic acid*, losing carbon as well as hydrogen; and concentrated nitric acid oxidizes it still further to *oxalic acid.*

Quartene glycol, $C_4H_{10}O_2$, is converted by slow oxidation with nitric acid into *oxybutyric acid*, $C_4H_8O_3$, and when the action is accelerated by heat, into *oxalic acid.* Quintene glycol, $C_5H_{12}O_2$, likewise yields *oxybutyric acid* by slow oxidation with dilute nitric acid.

2. *Potassium* and *sodium* eliminate one or two atoms of hydrogen from the glycols, and form substitution-products. Ethene alcohol is strongly attacked by sodium, yielding *sodium ethenate*, $C_2H_5NaO_2$; and this compound, fused with excess of sodium, is converted into *disodium ethenate*, $C_2H_4Na_2O_2$. These compounds, treated with monatomic alcoholic iodides, yield the alcoholic ethers of the glycols; thus,

$$\underset{\substack{\text{Sodium}\\\text{ethenate.}}}{\begin{matrix}CH_2ONa\\|\\CH_2OH\end{matrix}} + \underset{\substack{\text{Ethyl}\\\text{iodide.}}}{C_2H_5I} = \underset{\substack{\text{Sodium}\\\text{iodide.}}}{NaI} + \underset{\substack{\text{Ethyl}\\\text{ethenate.}}}{\begin{matrix}CH_2OC_2H_5\\|\\CH_2OH\end{matrix}}$$

$$\underset{\substack{\text{Disodium}\\\text{ethenate.}}}{\begin{matrix}CH_2ONa\\|\\CH_2ONa\end{matrix}} + \underset{\substack{\text{Ethyl}\\\text{iodide.}}}{2C_2H_2I} = \underset{\substack{\text{Sodium}\\\text{iodide.}}}{2NaI} + \underset{\substack{\text{Diethyl}\\\text{ethenate.}}}{\begin{matrix}CH_2OC_2H_5\\|\\CH_2OC_2H_5\end{matrix}}$$

3. *Oxygen acids*, heated with glycols in closed vessels, act upon them in the same manner as upon the monatomic alcohols, converting them into *ethereal salts* or *compound ethers*, mono-acid or di-acid, according to the pro-

portions used. In the di-acid glycol-ethers, the two radicals by which the hydrogen is replaced may belong either to the same or to different acids; *e. g.*,

$$\underset{\text{Ethene glycol.}}{CH_2OH\,|\,CH_2OH} + \underset{\text{Acetic acid.}}{HOC_2H_3O} = OH_2 + \underset{\text{Ethene mono-acetate.}}{CH_2OH\,|\,CH_2OC_2H_3O}$$

$$\underset{\text{Ethene glycol.}}{CH_2OH\,|\,CH_2OH} + \underset{\text{Acetic acid.}}{2HOC_2H_3O} = 2OH_2 + \underset{\text{Ethene di-acetate.}}{CH_2OC_2H_3O\,|\,CH_2OC_2H_3O}$$

$$\underset{\text{Ethene mono-acetate.}}{CH_2OH\,|\,CH_2OC_2H_3O} + \underset{\text{Butyric acid.}}{HOC_4H_7O} = OH_2 + \underset{\text{Ethene butyracetate.}}{CH_2OC_4H_7O\,|\,CH_2OC_2H_3O}$$

The *haloïd acids* act in the same manner as oxygen-acids, excepting that the reaction never goes beyond the first stage; *e. g.*,

$$\underset{\text{Ethene alcohol.}}{CH_2OH\,|\,CH_2OH} + HCl = OH_2 + \underset{\text{Ethene chloro-hydrate.}}{CH_2Cl\,|\,CH_2OH}$$

The bichlorinated, bibrominated ethers, &c., resulting from the substitution of the remaining equivalent of hydroxyl by the haloïd element, may, however, be obtained from the glycols by the action of the chlorides, bromides, and iodides of phosphorus; *e. g.*,

$$\underset{\text{Ethene alcohol.}}{C_2H_4(OH)_2} + \underset{\text{Phosphorus penta-chloride.}}{2PCl_5} = \underset{\text{Phosphorus oxy-chloride.}}{2PCl_3O} + \underset{\text{Hydrogen chloride.}}{2HCl} + \underset{\text{Ethene chloride.}}{C_2H_4Cl_2}$$

The same compounds are produced, as already observed, by direct combination of chlorine, bromine, and iodine with the olefines.

Ethene Chloride, $C_2H_4Cl_2$, has long been known by the name of *Dutch liquid*, having been discovered by four Dutch chemists in 1795. When equal measures of ethene gas and chlorine are mixed over water, absorption of the mixture takes place, and a yellowish oily liquid is produced, which collects upon the surface of the water, and ultimately sinks to the bottom in drops. It may be easily prepared, in quantity, by causing the two gases to combine in a glass globe, having a narrow neck at the lower part, dipping into a small bottle, destined to receive the product. The two gases are conveyed by separate tubes, and allowed to mix in the globe, the ethene gas being kept a little in excess. The chlorine should be washed with water, and the ethene passed through strong oil of vitriol, to remove vapor of ether: the presence of sulphurous and carbonic acids is not injurious. Combination takes place very rapidly, and the liquid product trickles down the sides of the globe into the receiver. When a considerable quantity has been collected, it is agitated, first with water, and afterward with concentrated sulphuric acid, and, lastly, purified by distillation.

Pure ethene chloride is a thin, colorless liquid, of agreeably fragrant odor, and sweet taste: it is slightly soluble in water, and readily so in alcohol and ether. It is heavier than water, and boils when heated to 82·3° C. (180° F.): it is unaffected by oil of vitriol, or solid potassium hydrate. When inflamed, it burns with a greenish, smoky light. When treated with an alcoholic solution of potash, it is slowly resolved into potassium chloride, which separates, and an exceedingly volatile substance, containing C_2H_3Cl, whose vapor requires to be cooled down to —18° C. (0° F.) before it condenses. At this temperature it forms a limpid, colorless liquid. Chlorine is absorbed by this latter substance, and a compound is produced, which contains $C_2H_3Cl_3$: this is in turn decomposed by an alcoholic solution of potash into potassium chloride and another volatile liquid, $C_2H_2Cl_2$. This series of reactions is analogous to that already noticed in the case of the bromine compounds (p. 465).

Fig. 192.

Products of the Action of Chlorine on Ethene Chloride; Chlorides of Carbon.—Ethene chloride readily absorbs chlorine gas, and yields four new compounds, produced by the abstraction of successive portions of hydrogen, and its replacement by equivalent quantities of chlorine. Three out of the four are volatile liquids, containing respectively, $C_2H_3Cl_3$, $C_2H_2Cl_4$, and C_2HCl_5; the fourth, C_2Cl_6, in which the substitution of chlorine for hydrogen is complete, is the *chloride of carbon* long ago obtained by Faraday by putting Dutch liquid into a vessel of chlorine gas, and exposing it to sunshine.

Carbon trichloride, C_3Cl_6, or $\begin{vmatrix} CCl_3 \\ CCl_3 \end{vmatrix}$, the chlorine analogue of ethane, C_2H_6, is a white, crystalline substance, of aromatic odor, insoluble in water, but easily dissolved by alcohol and ether: it melts at 160° C. (320° F.), and boils at a temperature a little above. It burns with difficulty, and is not altered by distillation with aqueous or alcoholic potash.

Its vapor, passed through a red-hot porcelain tube filled with fragments of glass or rock-crystal, is decomposed into free chlorine, and the *dichloride*, C_2Cl_4, analogous to ethene. This substance condenses in the form of a volatile, colorless liquid, which has a density of 1·55, and boils at 120° C. (248° F.). The density of its vapor is 5·82 (referred to air). When heated to 200° C. (392° F.) with potassium hydrate, it is completely converted into potassium chloride and oxalate, with evolution of hydrogen:

$$C_2Cl_4 + 6KOH = 4KCl + C_2K_2O_4 + 2OH_2 + H_2.$$

It absorbs chlorine and bromine in sunshine, forming in the one case the trichloride, C_2Cl_6, and on the other the chlorobromide, $C_2Cl_4Br_2$, a white crystalline body resembling the trichloride.

Carbon monochloride, C_2Cl_2, analogous to ethine or acetylene, is obtained by passing the vapor of chloroform or of carbon-dichloride through a red-hot tube. It forms white needles subliming between 175° and 200° C. (347° and 392° F.).

Carbon tetrachloride, CCl_4, may also be described in this place, though it belongs to another series, being the chlorine analogue to marsh-gas.

It is formed by passing the vapor of carbon bisulphide, together with chlorine, through a red-hot porcelain tube. A mixture of sulphur chloride

and carbon tetrachloride is formed, which is distilled with potash, whereby the chloride of sulphur is decomposed, and pure tetrachloride passes over. It is a colorless liquid of 1·56 sp. gr., and boils at 77° C (170° F.). The same compound is formed by exhausting the action of chlorine upon marsh-gas or methyl chloride in sunshine. An alcoholic solution of potash converts this compound into a mixture of potassium chloride and carbonate.

Ethene Bromide and Iodide, $C_2H_4Br_2$ and $C_2H_4I_2$, are produced by bringing olefiant gas in contact with bromine and iodine. The bromide is a colorless liquid, of agreeable ethereal odor, and has a density of 2·16: it boils at 129·5° C. (265° F.), and solidifies when cooled to near —18°. The iodide is a colorless, crystalline, volatile substance, of penetrating odor: it melts at 79° C. (174° F.), resists the action of sulphuric acid, but is decomposed by caustic potash.

The action of bromine upon ethene bromide gives rise to the compound $C_2H_3Br_3$, from which the other bromine-compounds corresponding to the chlorine bodies above mentioned may be obtained by treatment with bromine.

Ethene bromide acts strongly upon an alcoholic solution of *potassium sulph-hydrate*, forming *ethene sulph-hydrate* or *ethene mercaptan*, $C_2H_4(SH)_2$, a colorless oil, which is partially decomposed by distillation, and yields, with lead acetate, a yellow precipitate consisting of $C_2H_4S_2Pb$. With *potassium monosulphide*, in like manner, ethene bromide forms ethene sulphide, C_2H_4S, which crystallizes in white prisms.

The haloïd ethers corresponding to the higher glycols are similar in their reactions to those of ethene alcohol.

Oxygen Ethers of the Glycols.—The ethereal salts of the glycols (acetates, butyrates, &c.) are decomposed by alkalies in the same manner as those of the monatomic alcohols, reproducing the alcohols themselves: this is, in fact, the general mode of preparing the glycols (p. 556). But the mono-acid haloïd ethers of the glycols are decomposed by alkalies in a different manner, giving up the elements of hydrochloric, hydriodic, or hydrobromic acids, and leaving an *oxide* of the diatomic alcohol-radical; thus,

$$\underset{\text{Ethene chloro-hydrate.}}{(C_2H_4)''Cl(OH)} + KOH = KCl + OH_2 + \underset{\text{Ethene oxide.}}{(C_2H_4)''O}$$

Ethene oxide is isomeric with aldehyde and with vinyl alcohol (p. 484). It is a transparent colorless liquid, boiling at 13·5° C. (56° F.,) (aldehyde boils at 21° C. [70° F.]), and miscible in all proportions with water and with alcohol. When the aqueous solution is treated with *sodium amalgam*, in a vessel surrounded with a freezing mixture, the ethene oxide takes up hydrogen, and is converted into ethyl alcohol:

$$C_2H_4O + H_2 = C_2H_6O.$$

Ethene oxide unites with *ammonia* in several proportions, forming the following basic compounds, all of which are syrupy liquids:

Monoxethylenamine	$C_2H_4O.NH_3$
Dioxethylenamine	$(C_2H_4O)_2.NH_3$
Trioxethylenamine	$(C_2H_4O)_3.NH_3$
Tetroxethylenamine	$(C_2H_4O)_4.NH_3$.

This character distinguishes ethene oxide from aldehyde, which forms with ammonia a crystalline compound not possessing basic properties. A further distinction between these two isomeric bodies is, that aldehyde forms crystalline compounds with the acid sulphites of the alkali-metals, a property not possessed by ethene oxide.

Ethene oxide is a powerful base, uniting directly with *acids*, precipitating magnesia from a solution of magnesium chloride at ordinary temperatures, and ferric oxide and alumina from their saline solutions, at 100° C. With *hydrochloric acid*, it forms ethene chlorohydrate, $(C_2H_4)''\left\{\begin{matrix}Cl\\OH\end{matrix}\right.$, and with *acetic acid*, ethene acetohydrate, or monoacetate, $(C_2H_4)''\left\{\begin{matrix}OC_2H_3O\\OH.\end{matrix}\right.$ It also unites with *water* in several proportions, forming glycol and other compounds to be noticed immediately.

The oxygen-ethers of the higher glycols are not much known; but they appear to be less disposed to combine with water and acids in proportion as their molecules become heavier; thus amylene oxide does not appear to reproduce amylene alcohol by combination with water.

Polyethenic Alcohols. — These are bodies which contain the elements of two or more molecules of ethene oxide combined with one molecule of water, and may be regarded as formed by the union of two or more molecules of glycol (mono-ethenic alcohol), with elimination of a number of water-molecules less by one than the number of glycol molecules which enter into combination; or as derived from three or more molecules of water, by substitution of ethene for the whole of the hydrogen except two atoms; thus,

$C_2H_6O_2$ or $(C_2H_4)''H_2O_2$ (Monethenic alcohol (glycol).) $= C_2H_4O.OH_2$ (Ethene oxide.)

$C_4H_{10}O_3$ or $(C_2H_4)''_2H_2O_3$ (Diethenic alcohol.) $= 2C_2H_4O.OH_2$ (Ethene oxide.) $= 2C_2H_6O—OH_2$ (Glycol.)

$C_6H_{14}O_4$ or $(C_2H_4)''_3H_2O_4$ (Triethenic alcohol.) $= 3C_2H_4O.OH_2$ (Ethene oxide.) $= 3C_2H_6O—2OH_2$ (Glycol.)

$C_8H_{18}O_5$ or $(C_2H_4)''_4H_2O_5$ (Tetrethenic alcohol.) $= 4C_2H_4O.OH_2$ (Ethene oxide.) $= 4C_2H_6O—3OH_2$ (Glycol.)

Generally —

$C_{2n}H_{4n+2}O_{n+1}$ or $(C_2H_4)''_nH_2O_{n+1}$ (*n*-ethenic alcohol.) $= nC_2H_4O.OH_2$ (Ethene oxide.) $= nC_2H_6O—(n—1)OH_2$ (Glycol.)

The polyethenic alcohols are formed: 1. By heating ethene oxide with water in sealed tubes. In this manner Wurtz obtained diethenic alcohol together with monethenic, and a small quantity of tri-ethenic alcohol. — 2. By heating ethene oxide with glycol in sealed tubes: this process yields the di- and tri-ethenic alcohols. — 3. By heating glycol with ethene bromide in sealed tubes to 100°–120° C. (212°–248° F.). The first products of this reaction are diethenic alcohol, ethene bromo-hydrate and water:

$3(C_2H_4)''H_2O_2 + C_2H_4Br_2 = (C_2H_4)''_2H_2O_3 + 2(C_2H_4)''Br(OH) + OH_2$;
(Monethenic alcohol. — Ethene bromide. — Diethenic alcohol. — Ethene bromo-hydrate.)

and the other polyethenic alcohols are formed, each from the one next below it in the series, by the action of ethene bromo-hydrate, according to the general equation:

$$(C_2H_4)''_nH_2O_{n+1} + (C_2H_4)''Br(OH) = (C_2H_4)''_{n+1}H_2O_{n+2} + HBr.$$

The hydrobromic acid thus formed then acts on the excess of glycol present, reproducing ethene bromo-hydrate, and thus the action is continued. By this process, the 2-, 3-, 4-, 5-, and 6-ethenic alcohols have been obtained and separated by fractional distillation; and when a sufficient excess of glycol is present, the temperature being kept between 110° and 120° C. (230° and 248° F.), still higher members of the series are produced.*

The polyethenic alcohols are syrupy liquids, becoming more viscid as their molecular weight increases: their boiling point rises by about 45° for each addition of C_2H_4O.

Diethenic alcohol, $C_4H_{10}O_3$, or $(C_2H_4)''_2H_2O_3$, boils at about 245°; the density of its vapor is 3·78 referred to air as unity; by calculation it should be 3·67, so that it exhibits the normal condensation to two volumes. By contact with platinum-black, or by treatment with nitric acid, it is oxidized to *diglycollic acid*, $C_4H_6O_5$, an acid isomeric with malic acid, and formed from diethenic alcohol by substitution of O for H_2, just as glycollic acid, $C_2H_4O_3$, is formed from monethenic alcohol, C_2H_6O.—*Triethenic alcohol*, $C_6H_{14}O_4$, or $(C_2H_4)''_3H_2O_4$, is oxidized in like manner to *ethene-diglycollic acid*, $C_6H_{12}O_5$.

2.—Diatomic Phenols, $C_nH_{2n-6}O_2$.

There are five known compounds included in this general formula, viz.:

Oxyphenol or Pyrocatechin	$C_6H_6O_2$
Orcin Guaiacol (in part) }	$C_7H_8O_2$
Creosol Veratrol }	$C_8H_{10}O_2$

Oxyphenol, Oxyphenic Acid, or Pyrocatechin, $C_6H_6O_2$, or $(C_6H_4)''(OH)_2$, is produced by heating oxysalicylic acid to 210°–212°, just as phenol is produced from salicylic acid:

$$\underset{\text{Oxysalicylic acid.}}{C_7H_6O_4} = CO_2 + \underset{\text{Oxyphenol.}}{C_6H_6O_2};$$

also by the action of alkalies on iodophenol:

$$\underset{\text{Iodophenol.}}{C_6H_4I(OH)} + KOH = KI + \underset{\text{Oxyphenol.}}{C_6H_4(OH)_2}$$

It is likewise formed by the dry distillation of catechin (a substance obtained from catechu), of morintannic acid (the yellow coloring matter of *Morus tinctoria*), and of wood, whence it is found in wood vinegar: it does not occur in coal-tar. It is a white crystalline body, which melts at 111° or 112° C. (230°–233° F.), and volatilizes even at lower temperatures. It has a bitter taste, and scarcely reddens litmus. In contact with hydrochloric acid, it colors fir-wood violet. It dissolves in water, alcohol, and ether. The aqueous solution forms a white precipitate with *lead acetate*, and colors *ferric salts* dark-green. *Nitric acid* acts upon it with violence, forming oxalic acid and a small quantity of a yellow nitro-compound, probably nitro-oxyphenol. With *acetyl chloride* it forms acetoxyphenol, $C_6H_5(C_2H_3O)O_2$, and with *benzoyl chloride*, benzoxyphenol, $C_6H_5(C_7H_5O)O_2$, both of which are crystalline bodies.

Orcin, $C_7H_8O_2$.—This substance appears to exist ready formed in all the lichens (*Lecanora tartarea*, *Roccella tinctoria*, *Variolaria orcina*, &c.), which

* *Lourenzo*, Ann. Ch. Pharm. cxvii. 269.

are used for the preparation of archil and litmus; and is the general product of the decomposition of certain acids extracted from those lichens (orsellinic acid, erythric acid, &c) under the influence of heat or of alkalies. Orsellinic acid, $C_8H_8O_4$, when boiled with baryta-water, splits up into carbon dioxide and orcin, just as the homologous acid, oxysalicylic acid, $C_7H_6O_4$, splits up into carbon dioxide and oxyphenol (p. 562):

$$C_8H_8O_4 = CO_2 + C_7H_8O_2$$

Hence orcin appears to have the constitution of a diatomic phenol. To obtain the orcin, the excess of baryta is precipitated from the liquid by carbonic acid, and the filtrate evaporated to a small bulk. It forms, when pure, large square prisms, which have a slightly yellowish tint, an intensely sweet taste, and a high degree of solubility both in water and alcohol. When heated, it loses water, and melts to a syrupy liquid, which distils unchanged. The crystals of orcin contain $C_7H_8O_2 . OH_2$. It forms substitution-products with chlorine and bromine.

Orcein.—When ammonia is added to a solution of orcin, and the whole is exposed to the air, the liquid assumes a dark-red or purple tint by absorption of oxygen; a slight excess of acetic acid then causes the precipitation of a deep-red powder, not very soluble in water, but freely dissolved by ammonia and fixed alkalies, with a purple or violet color. This powder is an azotized substance, *orcein*, formed from the elements of the ammonia and the orcin; it probably constitutes the chief ingredient of the red dyestuff of the commercial articles before mentioned. Orcein probably contains $C_7H_7NO_3$, according to which formula, its formation from orcin, under the joint influence of oxygen and ammonia, may be represented by the equation:

$$C_7H_8O_2 + NH_3 + O_3 = C_7H_7NO_3 + 2OH_2.$$

Guaiacol and Creosol.—Guaiacum, a yellow or brown resin exuding from a West Indian tree (*Guaiacum officinale*), yields by dry distillation an oily liquid, which, when washed with water and rectified at a moderate heat, gives off, first, *guaiacene*, C_5H_8O, and afterward a colorless oil called *guaiacol*. This compound has a specific gravity of 1·119 at 22° C. (72° F.), and boils at 210° C. (410° F). It is soluble in alcohol, slightly soluble in water. *Nitric acid* converts it into oxalic acid and a brown resin. With *chlorine* and *bromine* it forms substitution-products. It dissolves in *potash*, and forms crystallizable salts with other bases. Guaiacol is not, however, a perfectly definite compound, but a mixture in varying proportions of the homologous compounds $C_7H_8O_2$ and $C_8H_{10}O_2$. The latter compound likewise exists in some kinds of wood-creosote: hence it is called *creosol*.

Creosote or Kreosote.—This substance, discovered by Reichenbach, is contained in many kinds of wood-tar, but most abundantly in the heavy oil of beech-tar, as obtained from the wood-vinegar makers. It is extracted and purified by a series of processes similar to those employed for the preparation of phenol or carbolic acid from coal-tar (p. 550).

Creosote is a colorless, somewhat viscid oily liquid, of great refractive and dispersive power. It is quite neutral to test-paper; has a penetrating and most peculiar odor, that, namely, of smoked meat, and a pungent and almost insupportable taste when placed even in very small quantity upon the tongue. Its density is 1·037, and its boiling-point about 203° C. (397° F). It takes fire with difficulty, and then burns with a smoky light. When quite pure, it is not altered by exposure to the air; but much of the creosote of commerce gradually turns brown under these circumstances. 100 parts of cold water take up about 1¼ part of creosote; at a high temperature rather more is dissolved, and the hot solution abandons a portion

on cooling. The creosote itself absorbs water also to a considerable extent. In acetic acid it dissolves in much larger quantity. Alcohol and ether mix with creosote in all proportions. Concentrated sulphuric acid, by the aid of heat, blackens and destroys it. Caustic potash dissolves creosote with great facility, and forms with it a compound, which crystallizes in brilliant pearly scales, and consists, according to Hlasiwetz,* of potassium creosolate, $C_8H_9KO_2.2OH_2$. When distilled with dilute sulphuric acid, it yields *creosol*, $C_8H_{10}O_2$. By treating creosote with potassium in an atmosphere of hydrogen, and crystallizing the product from ether, an acid potassium creosolate is obtained, consisting of $C_8H_9KO_2 . C_8H_{10}O_2$.

Hlasiwetz regards beech-tar creosote as an ether of creosol, represented either by the formula $C_8H_9RO_2$, or by $C_8H_9RO_2 . C_8H_{10}O_2$, in which R denotes a monatomic alcohol-radical. According to Frisch,† it consists mainly of acid phenylic creosol, $C_8H_9(C_6H_5)O_2 . C_8H_{10}O_2$. It may be distinguished from phenol by its behavior to ferric chloride, an alcoholic solution of that salt producing a green color with creosote and brown with phenol; an aqueous solution gives no color with creosote and a blue color with phenol. The creosote of commerce is, however, a substance of very variable constitution, much of it being nothing but impure phenols (commonly called *coal-tar creosote*). The tar of pine-wood, as already observed (p. 553), consists mainly of phenol and creosol.

The most characteristic property of wood-creosote is its extraordinary antiseptic power, which appears to be even greater than that of phenol. A piece of meat steeped in a very dilute solution of creosote dries up to a mummy-like substance, but absolutely refuses to putrefy. The well-known efficacy of impure wood-vinegar and of wood-smoke in preserving provisions is doubtless to be attributed to the creosote which they contain. Both creosote and phenol are used by the dentist for relieving toothache arising from putrefactive decay in the substance of the tooth.

Veratrol, $C_8H_{10}O_2$.—This compound is obtained by distilling veratric acid (an acid extracted from the seeds of *Veratrum Sabadilla*) with excess of baryta at a gentle heat, the mode of formation being that of the phenols in general from the corresponding acids of the series $C_nH_{2n-8}O_4$.

$C_9H_{10}O_4$	=	CO_2	+	$C_8H_{10}O_2$.
Veratric acid.				Veratrol.

Veratrol is a colorless oil having an agreeable aromatic odor, and specific gravity 1·086 at 15°; it solidifies at 15° C. (59° F.), and boils at 202°–205° C. (395°–401° F.). Bromine converts it into *dibromoveratrol*, $C_8H_8Br_2O_2$, which forms prismatic crystals. Nitric acid acts strongly upon it, forming *nitroveratrol*, $C_8H_9(NO_2)O_2$, which crystallizes from alcohol in yellow laminæ, and *dinitroveratrol*, $C_8H_8(NO_2)_2O_2$, which crystallizes in yellow needles, melting at 100°, and then volatilizing without decomposition.

Anisic Alcohol, $C_8H_{10}O_2$.—Crude anise oil, the essential oil of *Pimpinella Anisum*, contains a crystalline substance, $C_{10}H_{12}O$, called *anethol* or *anise camphor*. This substance when oxidized with nitric acid is converted into anisic aldehyde, $C_8H_8O_2$, which, when treated with alcoholic potash, takes up two atoms of hydrogen and is converted into *anisic alcohol*, $C_8H_{10}O_2$ (just as benzoic aldehyde, C_7H_6O, under similar circumstances yields benzyl alcohol, C_7H_8O; p. 548). Now this alcohol, though it contains two atoms of oxygen, nevertheless behaves, not like a diatomic, but like a monatomic alcohol, yielding only one series of ethers. The so-called anisic alcohol appears, indeed, to be really the methylic ether of the diatomic alcohol,

* Ann. Ch. Pharm. cvi. 339. † Journal für praktische Chemie, c. 283.

$C_7H_8O_2$, its formula being $C_7H_6(OCH_3)OH$; so that it contains only one atom of replaceable hydrogen. Hydrochloric acid gas converts it into the corresponding hydrochloric ether, $C_8H_9Cl(OH)$, or $C_7H_5(OCH_3)Cl(OH)$.

TRIATOMIC ALCOHOLS AND ETHERS.

Triatomic alcohols may be derived from saturated hydrocarbons by substitution of three equivalents of hydroxyl for three atoms of hydrogen, and may accordingly be regarded as compounds of trivalent alcohol radicals with three equivalents of hydroxyl, or as compounds derived from a triple molecule of water, by substitution of a trivalent radical for three atoms of hydrogen. The hydrocarbons of the paraffin series, C_nH_{2n+2}, should accordingly yield a series of triatomic alcohols of the form $(C_nH_{2n-1})'''(OH)_3$, viz.:—

Methenyl alcohol	$CH(OH)_3$
Ethenyl alcohol	$C_2H_3(OH)_3$
Propenyl alcohol	$C_3H_5(OH)_3$
Quartenyl alcohol	$C_4H_7(OH)_3$
Quintenyl alcohol	$C_5H_9(OH)_3$
&c.	&c.

Of these, however, only two are known, viz., *propenyl alcohol*, or *glycerin*, and *quintenyl alcohol*, or *amyl glycerin*. There are also two or three bodies which may be regarded as triatomic phenols, represented by the general formula $C_nH_{2n-6}O_3$, or $C_nH_{2n-9}(OH_3)$.

Each triatomic alcohol, subjected to the action of acids, or of the chlorides, bromides, or iodides of phosphorus, may yield three classes of ethers, derived from it by substitution of a halogen element, or acid radical, for part or the whole of the hydroxyl; thus, from glycerin may be obtained the three hydrochloric ethers, $C_3H_5Cl(OH)_2$, $C_3H_5Cl_2OH$, $C_3H_5Cl_3$, and the three acetic ethers, $C_3H_5(OC_2H_3O)(OH)_2$, $C_3H_5(OC_2H_3O)_2OH$, and $C_3H_5(OC_2H_3O)_3$.

Methenyl Ethers. — Methenyl alcohol, $CH(OH)_3$, has not been obtained; but ethers are known which may be derived from it, by substitution of halogen elements for the three equivalents of hydroxyl, $CHCl_3$ for example. These compounds, which may also be directly derived from methane, are usually distinguished by names ending in "form," to denote their relation to formic acid, $(CH)'''O(OH)$.

Methenyl Chloride or Chloroform, $CHCl_3$. — This compound is produced: 1. Together with methene chloride, CH_2Cl_2, when a mixture of chlorine and gaseous methyl chloride is exposed to the sun's rays. — 2. By the action of alkalies on chloral (p. 517):

C_2HCl_3O	+	KOH	=	$CHCl_3$	+	CHO_2K
Chloral.				Chloroform.		Potassium formate.

3. By boiling trichloracetic acid with aqueous alkalies:

$C_2HCl_3O_2$	+	2KOH	=	$CHCl_3$	+	CO_3K_2	+	OH_2
Trichloracetic acid.				Chloroform.		Potassium carbonate.		

4. By the action of nascent hydrogen on carbon tetrachloride:

$$CCl_4 + H_2 = HCl + CHCl_3.$$

5. By the action of hypochlorites, or of chlorine in presence of alkalies, on various organic substances, as methyl, ethyl, and amyl alcohols, acetic acid, acetone, &c. The reaction is complicated, giving rise to several other products; with common alcohol and calcium hypochlorite the principal reaction appears to be—

$$2C_2H_6O + 5Cl_2O_2Ca = 2CHCl_3 + 2CO_3Ca + 2CaCl_2 + CaH_2O_2 + 4OH_2.$$

Chloroform is prepared on the large scale by cautiously distilling together good commercial chloride of lime, water, and alcohol. The whole product distils over with the first portions of water, so that the operation may be soon interrupted with advantage. The chloroform, which constitutes the oily portion of the distillate, is purified by agitation with water, desiccation with calcium chloride, and distillation in a water-bath.

Chloroform is a thin, colorless liquid of agreeable ethereal odor, much resembling that of Dutch liquid, and of a sweetish taste. Its density is 1·48, and it boils at 61° C. (142° F.): the density of its vapor (compared with air) is 4·20. Chloroform is difficult to kindle, and burns with a greenish flame. It is nearly insoluble in water, and is not affected by concentrated sulphuric acid. When boiled with aqueous potash in a closed tube, it is converted into potassium chloride and formate:

$CHCl_3$	+	4HOK	=	3KCl	+	CHO(OK)	+	$2OH_2$
Chloroform.		Potassium hydrate.				Potassium formate.		

Chloroform is well known for its remarkable effects upon the animal system, in producing temporary insensibility to pain when its vapor is inhaled.

Bromoform, $CHBr_3$, is a heavy, volatile liquid, prepared by the simultaneous action of bromine and aqueous alkalies on alcohol, wood-spirit, and acetone. It is converted by caustic potash into potassium bromide and formate.

Iodoform, CHI_3, is a solid, yellow, crystallizable substance, easily obtained by adding alcoholic solution of potash to tincture of iodine, avoiding excess, evaporating the whole to dryness, and treating the residue with water. It is nearly insoluble in water, but dissolves in alcohol, and is decomposed by alkalies in the same manner as the preceding compounds. Bromine converts it into *bromiodoform*, $CHBr_2I$, a colorless liquid which solidifies at 0°. Iodoform distilled with phosphorus pentachloride or mercuric chloride, is converted into *chloriodoform*, $CHCl_2I$, a colorless liquid of sp. gr. 1·96, which does not solidify at any temperature. *Nitroform*, $CH(NO_2)_3$, a body analogous in composition to the methenyl ethers, will be considered in connection with the cyanogen compounds.

Propenyl Alcohol, or Glycerin,

$$C_3H_8O_3 = (C_3H_5)'''\begin{Bmatrix} OH \\ OH \\ OH \end{Bmatrix} \quad \text{or} \quad \begin{matrix} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{matrix}$$

This compound is obtained by the action of alkalies on natural fats, which are, in fact, the propenylic ethers of certain fatty acids; thus stearin, one of the constituents of mutton suet, consists of *propenyl tristearate*, $(C_3H_5)'''(OC_{18}H_{35}O)_3$, a compound derivable from glycerin itself, by substitution of stearyl, $C_{18}H_{35}O$, for hydrogen. Now, when stearin is boiled with a caustic alkali, it is converted into a stearate of the alkali-metal and glycerin, thus:

$$\underset{\text{Stearin.}}{C_3H_5(OC_{18}H_{35}O)_3} + 3KOH = \underset{\substack{\text{Potassium}\\\text{stearate.}}}{3KOC_{18}H_{35}O} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3}$$

A similar reaction takes place when any other similarly constituted fat is treated with a caustic alkali. The metallic salts of the fatty acids thus obtained are the well-known bodies called *soaps*, and the process is called *saponification;* this term, originally restricted to actual soap-making, has been extended to all cases of the resolution of a compound ether into an acid and an alcohol, such, for example, as the conversion of ethyl acetate into acetic acid and ethyl alcohol by the action of alcoholic potash.

Glycerin was originally obtained by heating together olive or other suitable oil, lead oxide, and water, as in the manufacture of common *lead-plaster;* an insoluble soap of lead is thereby formed, while the glycerin remains in the aqueous liquid. The latter is treated with sulphuretted hydrogen, digested with animal charcoal, filtered and evaporated in a vacuum at the temperature of the air. Glycerin is now produced in very large quantity and perfect purity in the decomposition of fatty substances by means of overheated steam, a process which Mr. George Wilson has lately introduced into the manufacture of candles.* In this reaction a fatty acid and glycerin are produced by assimilation of the elements of water; they are carried over by the excess of steam in a state of mechanical mixture, which rapidly separates into two layers in the receiver. The reaction is exactly similar to that which takes place when a caustic alkali is used to effect the saponification, *e. g.:*

$$\underset{\text{Stearin.}}{C_3H_5(OC_{18}H_{35}O)_3} + 3OH_2 = \underset{\text{Stearic acid.}}{3HOC_{18}H_{35}O} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3}$$

Glycerin may also be produced from propenyl bromide, $(C_3H_5)'''Br_3$, a compound formed, as already observed, by the action of bromine on allyl iodide, C_3H_5I. The process consists in converting the propenyl-bromide into propenyl triacetate, $(C_3H_5)'''(OC_2H_3O)_3$, by the action of silver acetate, and decomposing this compound ether with potash.

This mode of formation must not, however, be regarded as an actual synthesis of glycerin from compounds of simpler constitution; for the allyl-compounds are themselves prepared from glycerin (p. 544), and have never yet been obtained from any other source.

Glycerin is a nearly colorless and very viscid liquid, of sp. gr. 1·27, which cannot be made to crystallize. It has an intensely sweet taste, and mixes with water in all proportions: its solution does not undergo the alcoholic fermentation, but when mixed with yeast and kept in a warm place, it is gradually converted into propionic acid. Glycerin has no action on vegetable colors. Exposed to heat, it volatilizes in part, darkens, and decomposes, giving off, amongst other products, a substance called *acrolein*, C_3H_4O, having an intensely pungent odor.

Concentrated *nitric acid* converts glycerin into *glyceric acid*, $C_3H_6O_4$, an acid related to glycerin in the same manner as glycollic acid to glycol, and acetic acid to ethyl alcohol; being formed from it by substitution of oxygen for two atoms of hydrogen in immediate relation to hydroxyl; thus:

$$\underset{\substack{\text{Glycerin.}}}{\begin{matrix}CH_2OH\\|\\CHOH\\|\\CH_2OH\end{matrix}} + O_2 = OH_2 + \underset{\text{Glyceric acid.}}{\begin{matrix}CH_2OH\\|\\CHOH\\|\\COOH\end{matrix}}$$

* By Tilghman's process, an emulsion of water and fat is passed under pressure through a highly heated tube, and after delivery at the extreme end separates into a solution of glycerin and the fatty acid.—R. B.

The formula of glycerin indicates the possibility of effecting a second substitution of the same kind, which would yield diglyceric acid, $C_3H_4O_5$, but this acid has not been actually obtained.

Glycerin, treated with a mixture of strong nitric and sulphuric acids, forms *nitroglycerin*, $C_3H_5(NO_2)_3O_3$, a heavy oily liquid which explodes powerfully by percussion. It is much used for blasting in mines and quarries, but is very dangerous to handle, and has given rise to several fatal accidents.

Glycerin combines with the elements of sulphuric acid, forming a *sulphoglyceric acid*, $C_3H_8O_3SO_3$, which gives soluble salts with lime, baryta, and lead oxide.

Monatomic *oxygen acids* (acetic, benzoic, stearic, &c.), heated in sealed tubes with glycerin, yield compound ethers, in which 1, 2, or 3 hydrogen-atoms of the glycerin are replaced by an equivalent quantity of the acid radical, according to the proportions employed. The resulting compound ethers are denoted by names ending in *in;* thus:

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Acetic acid.}}{HOC_2H_3O} = \underset{\text{Mono-acetin.}}{C_3H_5(OH)_2OC_2H_3O} + OH_2$$

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Acetic acid.}}{2HOC_2H_3O} = \underset{\text{Diacetin.}}{C_3H_5(OH)(OC_2H_3O)_2} + 2OH_2$$

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + \underset{\text{Acetic acid.}}{3HOC_2H_3O} = \underset{\text{Triacetin.}}{C_3H_5(OC_2H_3O)_3} + 3OH_2$$

The glyceric ethers or *glycerides* thus produced are, for the most part, oily liquids increasing in viscidity as the acid from which they are formed has a higher molecular weight; those formed from the higher members of the fatty acid series, $C_n\,H_{2n}O_2$ (such as palmitic and stearic acids), are solid fats. Some of the triacid glycerides, produced artificially in the way just mentioned, are identical with natural fats occurring in the bodies of plants and animals; thus tristearin is identical with the stearin of beef and mutton suet; triolein with the olein of olive oil, &c.

Hydrochloric and *hydrobromic acids* act upon glycerin in the same manner as oxygen acids, excepting that the reaction always stops at the second stage (just as in the action of these acids on the glycols it stops at the first stage). The ethers thus formed are called *chlorhydrins* and *bromhydrins*, &c., *e. g.:*

$$\underset{\text{Glycerin.}}{C_2H_5(OH)_3} + HCl = \underset{\text{Chlorhydrin.}}{O_3H_5(OH)_2Cl} + OH_2$$

$$\underset{\text{Glycerin.}}{C_3H_5(OH)_3} + 2HCl = \underset{\text{Dichlorhydrin.}}{C_3H_5(OH)Cl_2} + 2OH_2$$

Hydriodic acid acts somewhat differently, producing an ether, $C_6H_{11}IO_3$, which may be regarded as a double molecule of glycerin, having four equivalents of hydroxyl replaced by two atoms of oxygen, and a fifth by iodine, $C_6H_{10}O_2(OH)I$.

The *chlorides* and *bromides of phosphorus* act upon glycerin in the same manner as hydrochloric and hydrobromic acid, but their action goes on to the third stage, producing trichlorhydrin or propenyl chloride and the corresponding bromine compound:

$$\underset{\text{Dichlorhydrin.}}{C_3H_5(OH)Cl_2} + PCl_5 = PCl_3O + HCl + \underset{\text{Trichlorhydrin.}}{C_3H_5Cl_3}$$

Iodide of phosphorus acts on glycerin in a totally different manner, yielding iodopropene or allyl iodide, C_3H_5I (p. 544).

Glycide.—When dichlorhydrin is treated with potash, it gives up a molecule of hydrochloric acid, and is converted into a compound called *epichlorhydrin*:

$$\underset{\text{Dichlorhydrin.}}{C_3H_5OHCl_2} - HCl = \underset{\text{Epichlorhydrin.}}{C_3H_5OCl}$$

This compound may be regarded as the hydrochloric ether of an alcohol, $C_3H_5O(OH)$, called glycide, formed from glycerin by abstraction of OH_2. Dibromhydrin, $C_3H_5(OH)Br_2$, treated in the same manner, yields *epibromhydrin*, or the hydrobromic ether of glycide, C_3H_5OBr. Epichlorhydrin heated with dry potassium iodide is converted into *epi-iodhydrin*, C_3H_5OI:

$$C_3H_5OCl + KI = KCl + C_3H_5OI.$$

These glycidic ethers are easily reconverted into bodies of the glycerin type. Thus epichlorhydrin combines with acetic acid, forming *glyceric acetochlorhydrin*:

$$\underset{\text{Epichlorhydrin.}}{(C_3H_5)'''ClO} + \underset{\text{Acetic acid.}}{HOC_2H_3O} = \underset{\text{Acetochlorhydrin.}}{(C_3H_5)'''Cl(OH)(OC_2H_3O)};$$

and with alcohol, in like manner, forming *glyceric ethylchlorhydrin*, $(C_3H_5)'''Cl(OH)(OC_2H_5)$.

Epichlorhydrin unites directly with *water*, forming *glyceric monochlorhydrin*, $C_3H_5(OH)_2Cl$.

Polyglycerins.—Two, three, or more molecules of glycerin can unite into a single molecule, with elimination of a number of water molecules less by one than the number of glycerin molecules which combine together; thus:

$$\underset{\text{Glycerin.}}{2C_3H_5(OH)_3} - OH_2 = (C_3H_5)'''_2\left\{\begin{matrix}O'' \\ (OH)_4\end{matrix}\right. \quad \text{Diglycerin.}$$

$$\underset{\text{Glycerin.}}{3C_3H_5(OH)_3} - 2OH_2 = (C_3H_5)'''_3\left\{\begin{matrix}O''_2 \\ (OH)_5\end{matrix}\right. \quad \text{Triglycerin.}$$

Generally:

$$nC_3H_5(OH)_3 - (n-1)OH_2 = (C_3H_5)_n\left\{\begin{matrix}O_{n-1} \\ (OH)_{n+2}\end{matrix}\right.$$

The product is a polyglycerin whose atomicity (determined by the number of equivalents of hydroxyl contained in it) is $n+2$.

The mode of preparing the polyglycerins is similar to that of the polyethenic alcohols (p. 561), and consists in heating glycerin with chlorhydrin, whereby diglycerin and hydrochloric acid are formed:

$$\underset{\text{Chlorhydrin.}}{C_3H_5Cl(OH)_2} + \underset{\text{Glycerin.}}{C_3H_5(OH)_3} = \underset{\text{Diglycerin.}}{(C_3H_5)_2O(OH)_4} + HCl$$

The hydrochloric acid thus formed converts a fresh quantity of glycerin into chlorhydrin, which then acts in a similar manner on the diglycerin and converts it into triglycerin, and in this manner the process is continued. The polyglycerins may then be separated by fractional distillation. Their properties are but little known.

Quintenyl Alcohol, or Amyl Glycerin, $C_5H_{12}O_3=(C_5H_9)'''(OH)_3$.—This compound is formed from bromoquintene dibromide, $C_5H_9Br \cdot Br_2$, or quintenyl bromide, $C_5H_9Br_3$, by the series of processes represented in the following equations:

$$\underset{\text{Quintenyl bromide.}}{C_5H_9Br_3} + 2AgOC_2H_3O = \underset{\text{Silver bromide.}}{2AgBr} + \underset{\text{Quintenyl diaceto-bromhydrin.}}{(C_5H_9)'''\left\{\begin{matrix}(OC_2H_3O)_2\\Br\end{matrix}\right.}$$

$$\underset{\text{Quintenyl diaceto-bromhydrin.}}{(C_5H_9)'''\left\{\begin{matrix}(OC_2H_3O)_2\\Br\end{matrix}\right.} + \underset{\text{Potassium hydrate.}}{2KOH} = \underset{\text{Potassium acetate.}}{2KOC_2H_3O} + \underset{\text{Quintenyl bromhydrin.}}{C_5H_9'''\left\}\begin{matrix}(OH)_2\\Br\end{matrix}\right.}$$

$$\underset{\text{Quintenyl bromhydrin.}}{(C_5H_9)'''\left\{\begin{matrix}(OH)_2\\Br\end{matrix}\right.} + KOH = KBr + \underset{\text{Quintenyl alcohol.}}{(C_5H_9)'''(OH)_3}$$

Quintenyl alcohol is a thick colorless liquid, having a sweet aromatic taste, and soluble in water.*

Triatomic Phenols.

There are three compounds represented by the formula $C_6H_6O_3$, and exhibiting a certain relationship to the phenols; these are:

1. *Pyrogallol*, or *Pyrogallic acid*, produced by the action of heat on gallic (dioxysalicylic) acid:

$$\underset{\text{Gallic acid.}}{C_7H_6O_5} = CO_2 + \underset{\text{Pyrogallic acid.}}{C_6H_6O_3};$$

also, together with gallic acid, by the action of hot caustic potash on diiodo salicylic acid, $C_7H_4I_2O_3$. It is conveniently prepared by heating a dried aqueous extract of gall-nuts to 180°–185° C. (356°–365° F.) in an iron pot covered with a paper cap. It then sublimes and condenses on the cap in long flattened prisms.

Pyrogallic acid is soluble in water, alcohol, and ether; it melts at 115° C. (239° F.), boils at 210° C. (410° F.), and decomposes at 250° C. (482° F.), giving off water and leaving a residue of *metagallic acid*, $C_6H_4O_2$. It dissolves in caustic potash or soda, forming a solution which quickly absorbs oxygen from the air, and turns black: this solution forms a very convenient reagent for the eudiometric analysis of air (p. 155). With solutions of pure ferrous salts it produces a fine blue color, but the smallest trace of ferric salt changes the tint to green. With bromine, pyrogallic acid forms a substitution-product containing $C_6H_3Br_3O_3$.

2. *Phloroglucin.* — Phlorizin, or phloridzin, a crystalline substance, existing ready-formed in the root-bark of the apple, pear, plum, and cherry-trees, is resolved by boiling with dilute acids into glucose, and another crystalline substance, phloretin:

$$\underset{\text{Phlorizin.}}{C_{21}H_{24}O_{10}} + OH_2 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Phloretin.}}{C_{15}H_{14}O};$$

and phloretin, treated with aqueous potash, is resolved into phloretic acid, and phloroglucin:

$$\underset{\text{Phloretin.}}{C_{15}H_{14}O_5} + OH_2 = \underset{\text{Phloretic acid.}}{C_9H_{10}O_3} + \underset{\text{Phloro-glucin.}}{C_6H_6O_3}$$

Phloroglucin is a neutral crystalline substance, having a very sweet taste, soluble in water, alcohol, and ether. With *bromine* it forms the com-

* *Bauer*, Zeitschrift für Chem. u. Pharm. 1861, p. 673.

pound $C_6H_3Br_3O_3$; with *nitric acid*, $C_6H_5(NO_2)O_3$; with *ammonia*, a base called *phloramine*, $C_6H_5(NH_2)O_2$; with *acetyl chloride* and *benzoyl chloride*, it yields the compounds $C_6H_5(C_2H_3O)O_3$, and $C_6H_5(C_7H_5O)O_3$, both of which are crystalline.

3. *Frangulin.* — This is a yellow crystallizable substance, contained in the bark of the berry-bearing alder (*Rhamnus frangula*). It is insoluble in water, slightly soluble in warm alcohol and ether, soluble in fixed oils, benzene, and oil of turpentine. Fuming nitric acid dissolves it, forming oxalic acid, and an acid called *nitrofrangulic acid*, said to contain $C_{20}H_{11}N_5O_{18}$.

TETRATOMIC ALCOHOLS AND ETHERS.

The only tetratomic alcohols at present known are erythrite, $C_4H_{10}O_4$, and propylphycite, $C_3H_8O_4$.

Erythrite, $C_4H_{10}O_4=(C_4H_6)^{iv}(OH)_4$, also called *Erythromannite*, *Erythroglucin*, and *Phycite*, is the tetratomic alcohol corresponding to quartyl alcohol, $C_4H_{10}O$, and quartyl glycol, $C_4H_{10}O_2$; the corresponding glycerin is not known.

Erythrite is a saccharine substance, existing ready-formed in *Protococcus vulgaris*. It was originally discovered by Dr. Stenhouse among the products of decomposition of erythric acid.* It crystallizes in large transparent prisms, is readily soluble in water, sparingly soluble in alcohol, insoluble in ether; not fermentable. Heated with *hydriodic acid*, it yields secondary quartyl iodide, C_4H_9I (p. 534):

$$C_4H_{10}O_4 + 7HI = C_4H_9I + 4OH_2 + 3I_2.$$

Heated with *oxygen acids*, it forms compound ethers, in the manner of alcohols in general; thus, with *benzoic acid*, $C_7H_6O_2$, or HOC_7H_5O, it forms a dibenzoate, $(C_4H_6)^{iv}(OH)_2(OC_7H_5O)_2$, and a hexbenzoate, $(C_4H_6)^{iv}(OC_7H_5O)_4$. $2C_7H_6O_2$, consisting of neutral benzoyl-erythrite united with two molecules of benzoic acid.

Propylphycite, $C_3H_8O_4=(C_3H_4)^{iv}(OH)_4$. — This alcohol is obtained synthetically by the following series of processes: 1. Epichlorhydrin which combines with hypochlorous acid, forming the dichlorhydrin of propylphycite:

C_3H_5OCl	+	ClOH	=	$(C_3H_4)^{iv}Cl_2(OH)_2$
Epichlorhydrin.		Hypochlorous acid.		Dichlorhydrin of propylphycite.

2. This dichlorhydrin, treated with silver acetate, is converted into the corresponding diacetin, $(C_3H_4)^{iv}(OC_2H_3O)_2(OH)_2$. — 3. The diacetin, heated with aqueous potash, yields the tetratomic alcohol.

Propylphycite is a colorless, solid, amorphous mass, which deliquesces in the air to a glutinous liquid. It has a sweetish taste, dissolves easily in alcohol, and resembles erythrite in its chemical relations. With fuming nitric acid, it forms *nitropropylphycite*, $C_3H_7(NO_2)O_4$.

Carbon tetrachloride, CCl_4, may be regarded as a tetratomic ether; the corresponding alcohol, $C(OH)_4$, is theoretically possible, but is not actually known.

* See the chapter on coloring matters.

PENTATOMIC ALCOHOLS.

Pinite and *quercite*, two saccharine substances having the composition $C_6H_{12}O_5$, probably belong to this class of bodies, inasmuch as they produce ethers when treated with acids, and the atomicity of an alcohol — that is to say, the number of replaceable hydrogen-atoms which it contains — is equal to the number of oxygen-atoms in its molecule; such indeed is the case with all the alcohols described in the preceding pages.

Pinite is contained in the sap of a Californian pine (*Pinus Lambertiana*), and is deposited from the aqueous extract of the hardened juice, in hard white crystalline nodules, as sweet as sugar-candy, very soluble in water, nearly insoluble in alcohol. It turns the plane of polarization of a luminous ray to the right; is not fermentable. With *benzoic acid* it forms *dibenzopinite*, $C_6H_7(OC_7H_5O)_2(OH)_3$, and *tetrabenzopinite*, $C_6H_7(OC_7H_5O)_4(OH)$; and similar compounds with *stearic acid*.

Quercite is a saccharine substance extracted from acorns, by treating the aqueous infusion with milk of lime to remove tannic acid, leaving the liquid to ferment with yeast to remove fermentable sugar, evaporating the filtrate to a syrup, and leaving it to crystallize. It forms hard monoclinic crystals, which grate between the teeth, and are soluble in water and in hot dilute alcohol. Heated in a sealed tube with *benzoic acid*, it forms *dibenzoquercite*, $C_6H_7(OC_7H_5O)_2(OH)_3$.

HEXATOMIC ALCOHOLS AND ETHERS.

This class of compounds includes most of the saccharine substances found in plants, and others produced from them by artificial transformation. Two of the natural sugars, *mannite* and *dulcite*, having the composition $C_6H_{14}O_6$, or $(C_6H_8)^{vi}(OH)_6$, are saturated hexatomic alcohols derived from the saturated hydrocarbon, C_6H_{14}. Several others, called *glucoses*, contain $C_6H_{12}O_6$, that is to say, two atoms of hydrogen less than mannite and dulcite, and may therefore be regarded — so far as composition is concerned — as the aldehydes of these alcohols; moreover, ordinary glucose (grape-sugar) is converted into mannite by the action of nascent hydrogen, just as acetic aldehyde, C_2H_4O, is converted into common alcohol, C_2H_6O. Further, there are *diglucosic alcohols*, $C_{12}H_{22}O_{11}(= 2C_6H_{12}O_6 - OH_2)$, related to the glucoses in the same manner as diethenic alcohol to glycol, or diglycerin to glycerin: the most important of these are *cane-sugar* and *milk-sugar;* and, lastly, there are certain vegetable products — viz., *starch*, *cellulose*, and a few others, represented by the formula $C_6H_{10}O_5$, or multiples thereof which may be regarded as the oxygen-ethers or anhydrides of the glucoses, or of the diglucosic alcohols, inasmuch as they differ therefrom by a molecule of water.

SATURATED HEXATOMIC ALCOHOLS.

Mannite, $C_6H_{14}O_6 = (C_6H_8)(OH)_6$. — This is the chief component of *manna*, an exudation from a species of ash: it is also found in the juice of certain other plants, in several sea-weeds, and in mushrooms. It is best prepared by treating manna with boiling alcohol, and filtering the solution while hot; it then crystallizes on cooling in tufts of slender needles. Mannite may be produced artificially by treating a solution of glucose with sodium amalgam, the glucose then taking up 2 atoms of hydrogen:

$$C_6H_{12}O_6 + H_2 = C_6H_{14}O_6.$$

The same transformation of glucose sometimes takes place under the action of certain ferments.

Mannite crystallizes in thin four-sided prisms, easily soluble in water and in hot alcohol, insoluble in ether. It is slightly sweet, has no action on polarized light, and is not fermentable except under very unusual conditions.

By oxidation in contact with *platinum-black*, mannite is converted into *mannitic acid*, $C_6H_{10}O_7$, and *mannitose*, $C_6H_{12}O_6$, a kind of sugar isomeric with glucose. By oxidation with *nitric acid* it yields *saccharic acid*, C_6H_{10}, and ultimately *oxalic acid*. Mannitic acid and saccharic acid are related to mannite in the same manner as glycollic acid and oxalic acid to glycol; the relation between the three compounds is shown by the following formulæ:

Mannite.	Mannitic acid.	Saccharic acid.
CH_2OH	COOH	COOH
|	|	|
CHOH	CHOH	CHOH
|	|	|
CHOH	CHOH	CHOH
|	|	|
CHOH	CHOH	CHOH
|	|	|
CHOH	CHOH	CHOH
|	|	|
CH_2OH	CH_2OH	COOH

By *fuming nitric acid*, or more easily by a mixture of *nitric* and *sulphuric acids*, mannite is converted into *nitromannite*, $C_6H_8(NO_2)_6O_6$, a crystalline body, which explodes violently by percussion or when suddenly heated, and is reconverted into mannite by ammonium sulphide. With sulphuric acid mannite forms *sulpho-mannitic acid*, $C_6H_{14}O_6 . 3SO_3$.

Mannite, treated with *hydriodic acid*, is converted into secondary hexyl iodide, or hexylene hydriodide (p. 539):

$$\underset{\text{Mannite.}}{C_6H_{14}O_6} + 11HI = \underset{\substack{\text{Hexyl}\\\text{iodide.}}}{C_6H_{13}I} + 6OH_2 + 5I_2$$

Mannite, heated with *organic acids*, forms compound ethers, after the manner of alcohols in general, the elements of the mannite and the acid uniting together, with elimination of one or more molecules of water. The resulting compounds, called *mannitanides*, bear a considerable resemblance to the fats; but their composition has not been very exactly determined.

These ethers, when saponified with alkalies, yield, not mannite, but *mannitan*, $C_6H_{12}O_5$, a compound differing from mannite by one molecule of water. The same compound is obtained in small quantity by heating mannite to 200° C. (392° F.), and more easily by prolonged boiling of mannite with strong hydrochloric acid. It is a syrupy liquid, which volatilizes slowly at 140° C. (284° F.), and dissolves easily in water and in cold absolute alcohol: this last property affords the means of separating it from mannite. When exposed to the air, it slowly absorbs water, and is reconverted into mannite; the change is accelerated by boiling with acids or with alkalies.

Mannite, boiled with *butyric acid*, gives up two molecules of water, and is converted into *mannide*, $C_6H_{10}O_4$, which is also a syrupy liquid, but differs from mannitan in being much more volatile, evaporating rapidly at 140°, and in being quickly reconverted into mannite by exposure to moist air. It dissolves easily in water and in absolute alcohol.

Dulcite, $C_6H_{14}O_6$, also called *Dulcin*, *Dulcose*, and *Melampyrite*.—This sugar,

isomeric with mannite, is obtained from a crystalline substance, of unknown origin, imported from Madagascar: it is extracted therefrom by boiling with water, and crystallizes from the filtered solution. Dulcite is likewise obtained from *Melampyrum nemorosum*, by mixing the aqueous decoction of the plant with lime, concentrating, adding hydrochloric acid in slight excess, and evaporating a little; it then separates in crystals as the liquid cools.

Dulcite is a sweet substance resembling mannite in most of its properties, but differing from it in its crystalline form, which is that of a monoclinic prism, whereas the crystals of mannite are trimetric; and also in its melting point, dulcite melting at 182° C. (360° F.), mannite at 165° C. (329° F.), and by yielding, when oxidized with nitric acid, not saccharic acid, but mucic acid, which is isomeric therewith. Heated with organic acids, it forms ethers called dulcitanides, analogous to the *mannitanides*, and yielding by saponification, not dulcite, but *dulcitan*, $C_6H_{12}O_5$, which may likewise be obtained by heating dulcite or by boiling it with hydrochloric acid.

Isodulcite, $C_6H_{14}O_6$, or $C_6H_{12}O_5 . OH_2$, a saccharine substance isomeric with mannite and dulcite, is produced, according to Hlasiwetz and Pfaundler,* by the action of dilute acid on quercitrin (p. 000). It forms large transparent, regularly developed crystals resembling those of cane-sugar: it is sweeter than grape-sugar, not fermentable, dissolves in 2·09 parts of water at 18° C. (64° F.), and easily in absolute alcohol. The solutions turn the plane of polarization to the right. Isodulcite melts with loss of water between 105° and 110° C. (221°–230° F.), is colored yellow or brown by strong sulphuric acid and caustic alkalies, and reduces cupric oxide. By a mixture of nitric and sulphuric acids, it is converted into a slightly explosive nitro-compound, $C_6H_9(NO_2)_3O_5$.

GLUCOSES, $C_6H_{12}O_6$.

The sugars included in this formula may be regarded as aldehydes of the saturated alcohols, $C_6H_{14}O_6$. Ordinary glucose (grape-sugar) is converted into mannite by the action of nascent hydrogen (p. 572), and, on the other hand, mannite when slowly oxidized in contact with platinum black is partly converted into mannitose. Nevertheless, the glucoses still exhibit the characteristic property of alcohols, namely, that of forming ethers by combination with acids and elimination of water. The formula of a glucose may indeed be derived from that of mannite given on page 573, by removing two hydrogen-atoms from one of the groups, CH_2OH, the other groups remaining as before; the glucoses may therefore be expected to act as pentatomic alcohols. Bodies thus constituted may be called *alcoholic aldehydes*.

The following varieties of glucose are known:

1. *Ordinary glucose*, produced by hydration of starch under the influence of dilute acids or of diastase, and existing ready-formed, together with other kinds of sugar, in honey and various fruits, especially in grapes, and alone in diabetic urine.

2. *Maltose*, produced by the limited action of diastase on starch, and differing from glucose only in its optical rotatory power.

3. *Levulose*, existing in cane-sugar which has been acted upon by acids, and obtained pure by the action of dilute acids upon a variety of starch called inulin.

4. *Mannitose*, produced by oxidation of mannite.

5. *Galactose*, formed by the action of acids on milk-sugar.

* Ann. Ch. Pharm. cxxvii. 362.

6. *Inosite*, existing in muscular flesh.
7. *Sorbin*, obtained from mountain-ash berries.
8. *Eucalyn*, existing, together with another kind of sugar, in the so-called Australian manna.

The first four of these glucoses exhibit but very slightly diversity in their chemical properties, differing chiefly indeed in their action on polarized light, and a few other physical properties. They all yield saccharic acid by oxidation. Galactose differs from them in yielding mucic acid when oxidized. Inosite, sorbin, and eucalyn exhibit still greater differences in their chemical properties, especially in not being fermentable except under very peculiar circumstances, whereas the five other glucoses undergo vinous fermentation when placed under certain conditions in contact with yeast.

All the glucoses, except inosite, are decomposed by boiling with aqueous alkalies; this property distinguishes them from mannite and dulcite. They are not carbonized by strong sulphuric acid at ordinary temperatures. When boiled with a solution of potassio-cupric tartrate, they throw down the copper in the form of red cuprous oxide.

1. **Ordinary Glucose, Dextro-glucose, Dextrose,** $C_6H_{12}O_6 . OH_2$. — This variety of sugar is very abundantly diffused through the vegetable kingdom: it may be extracted in large quantity from the juice of sweet grapes (whence it is often called *grape-sugar*), and also from honey, of which it forms the solid crystalline portion, by washing with cold alcohol, which dissolves the fluid syrup. The appearance of this substance, to an enormous extent, in the urine, is the most characteristic feature of the disease called *diabetes*. It exists in diabetic urine unmixed with any other kind of sugar, and is easily obtained by concentrating the liquid till it crystallizes, washing the crystals with cold alcohol, dissolving them in water, and re-crystallizing. It may also be prepared from starch by the action of diastase, a peculiar ferment existing in germinating barley, or by boiling with dilute sulphuric acid. In these reactions the starch takes up the elements of water, and is resolved into glucose and dextrin, a compound isomeric with starch itself, the transformation being exactly similar to the saponification of a fat under the influence of alkalies:

$3C_6H_{10}O_5$	+	OH_2	=	$C_6H_{12}O_6$	+	$2C_6H_{10}O_5$
Starch.				Glucose.		Dextrin.

Glucose is always prepared from starch when required in considerable quantity. The mode of preparation will be described in connection with starch. Cellulose is likewise converted into glucose by the action of acids (p. 000). Lastly, glucose is produced by the decomposition of natural glucosides by boiling with dilute acids.

Glucose is much less sweet than cane-sugar, and less soluble in water, requiring $1\frac{1}{2}$ parts of the cold liquid for solution. It separates from its solutions in water and alcohol in granular warty masses, which but seldom present crystalline faces. When pure, it is nearly white. In the state of solution it turns the plane of polarization of a ray of light to the right (hence the name *dextro-glucose* and *dextrose*): its specific or molecular rotatory power* is + 56°, and does not vary with the temperature.

Glucose may be heated to 120° or even 130° C. (248°–256° F.) without

* The specific or molecular rotatory power of an optically active substance, usually denoted by the symbol $[a]$, is measured by the number of degrees through which a column 100 millimetres or 1 decimetre thick, of a solution containing 1 gram of the pure substance, would rotate the plane of polarization, supposing the specific gravity of the solution to be = 1. Hence, if the molecular rotatory power $[a]$ is known, the rotation, a, of the plane of polarization caused by a stratum 1 decimetre thick, of a solution of sp. gr. 1, and containing ε grams of substance in 1 gram of solution, is expressed by the equation, $a = \varepsilon [a]$. If, however, the sp.

alteration, but at 170° C. (338° F.) it gives off water and is converted into *glucosan*, $C_6H_{10}O_5$, which, when freed from caramel (p. 000) by means of charcoal, and from glucose by fermentation, forms a colorless mass, scarcely sweet to the taste, and having somewhat less dextro-rotatory power than glucose. At higher temperatures glucose blackens and suffers complete decomposition. Glucose boiled for some time with *dilute sulphuric* or *hydrochloric acid*, is converted into brown substances called ulmin, ulmic acid, &c. — *Strong sulphuric acid* converts it at ordinary temperatures into sulphosaccharic acid, $C_6H_{12}O_5SO_3$, which forms a soluble barium salt.

Lime, *baryta*, and *lead oxide* dissolve slowly in aqueous solution of glucose, and on adding alcohol to the liquid, compounds of these oxides with glucose are precipitated. The barium compound is said to contain $(C_2H_{12}O_6)_2(BaO)_3.2OH_2$; the calcium compound, $(C_6H_{12}O_6)_2(CaO)_3.2OH_2$; the lead compound, $(C_6H_{12}O_6)^{vi}{}_2(PbO)_3(OH)_6$. These compounds are, however, very unstable, being decomposed at the heat of boiling water. Glucose also combines with *sodium chloride*, forming the compound $(C_6H_{12}O_6)_2NaCl.OH_2$.

Glucose, boiled with a *cupric salt* in presence of *alkalies*, easily reduces the cupric oxide to cuprous oxide: by this character it is easily distinguished from cane-sugar.

When solutions of cane-sugar and glucose are mixed with two separate portions of solution of cupric sulphate, and caustic potash added in excess to each, deep-blue liquids are obtained, which, on being heated, exhibit different characters; the one containing cane-sugar is at first but little altered; a small quantity of red powder falls after a time, but the liquid long retains its blue tint: with the glucose, on the other hand, the first application of heat throws down a copious greenish precipitate, which rapidly changes to scarlet, and eventually to dark-red cuprous oxide, leaving a nearly colorless solution. If the analyst have but small quantities of material at his disposal, a mixture of cupric sulphate and tartaric acid, to which an excess of potash has been added, may be used with advantage. This solution, called *potassio-cupric tartrate*, is an excellent test for distinguishing the two varieties of sugar, or discovering an admixture of glucose with cane-sugar.

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gr. is δ, we have $\alpha = \varepsilon[\alpha]\delta$. If the thickness of the stratum is λ decimetres, we have finally:

$$\alpha = \varepsilon[\alpha]\delta\lambda.$$

If, then, the angle of rotation, α, has been found by experiment, the quantity of substance, ε, in 1 gram of solution is given by the equation,

$$\varepsilon = \frac{\alpha}{[\alpha]\delta\lambda.}$$

If, on the other hand, it is desired to determine the specific rotatory power, we have the equation,

$$[\alpha] = \frac{\alpha}{\varepsilon\delta\lambda.}$$

For example, by dissolving 11·347 grams of dextro-glucose in 88·653 grams of water, a solution is obtained, having a sp. gr. of 1·048, and producing in a tube 2 decimetres long, a rotation of 13·7°. Hence the molecular rotatory power of dextro-glucose is given by the equation,

$$[\alpha] = \frac{13{\cdot}7}{0{\cdot}11347 \times 2 \times 1{\cdot}048.} = 57{\cdot}6.$$

The rotation is generally observed for the *transition tint* between the blue and the purple, in which case the molecular rotatory power is denoted by the simple symbol $[\alpha]$; sometimes, however, it is observed for the red ray; and in this case the symbol $[\alpha]r$ is employed. The rotation is distinguished as + or —, according as it takes place to the right or the left.

Glucose mixed in dilute solution with *yeast* and exposed to a temperature of 21°–26° C. (70°–80° F.), easily undergoes vinous fermentation (p. 516).

2. **Maltose**, $C_6H_{12}O_6$.—This name is given by Dubrunfaut to the sugar produced by the action of diastase upon starch. It has a dextro-rotatory power three times as great as that of ordinary glucose, but resembles the latter in all other respects, and is converted into it by boiling with dilute acids. It appears to be merely a physical modification of glucose, the difference between the two depending on the arrangement of the molecules, not on that of the atoms within a molecule.

3. **Levulose**, $C_6H_{12}O_6$.—This sugar, distinguished from dextro-glucose by turning the plane of polarization to the left, occurs, together with dextro-glucose, in honey, in many fruits, and in other saccharine substances. The mixture of these two sugars in equivalent quantities constitutes *fruit-sugar*, or *inverted sugar*, which is itself levorotatory, because the specific rotatory power of levulose is, at ordinary temperatures, greater than that of dextro-glucose.

Cane-sugar may be *inverted*, that is, transformed into a mixture of equal parts of dextro-glucose and levulose, by warming with dilute acids:

$$C_{12}H_{22}O_{11} + OH_2 = C_6H_{12}O_6 + C_6H_{12}O_6.$$

The same change is brought about by contact with yeast, or with pectase, the peculiar ferment of fruits; and likewise takes place slowly when a solution of cane-sugar is left to itself.

To separate the levulose, the inverted sugar obtained from 10 grams of cane-sugar is mixed with 6 grams of slaked lime and 100 grams of water, whereby a solid calcium-compound of levulose is formed, while the whole of the dextro-glucose remains in solution, and may be separated from the precipitate by pressure. The calcium salt of levulose suspended in water and decomposed by carbon dioxide, yields a solution of pure levulose, which may be filtered and concentrated by evaporation. Levulose may be at once obtained in the pure state by the action of dilute acids on inulin.

Levulose is a colorless uncrystallizable syrup, as sweet as cane-sugar, more soluble in alcohol than dextro-glucose. Its rotatory power is much greater than that of dextro-glucose at ordinary temperatures, but diminishes as the temperature rises. For the transition tint, $[\alpha] = -106°$ at 14° C. (57° F.); $= -79{\cdot}5°$ at 52° C. (122° F.), $= -53°$ at 90° C. (194° F.). Now, the rotatory power of dextro-glucose is the same at all temperatures, and equal to $+56°$; consequently that of inverted sugar, which is $-25°$ at 15°, diminishes by about one-half at 52°, becomes nothing at 90°, and changes sign above that temperature.

Levulose exhibits, for the most part, the same chemical reactions as dextro-glucose, but is more easily altered by heat or by acids, and on the contrary offers greater resistance to the action of alkalies or of ferments.

Levolusan, $C_6H_{10}O_5$, the oxygen-ether or anhydride of levulose, is produced, together with dextro-glucose, by melting cane-sugar for some time at 160° C. (32° F.):

$$C_{12}H_{22}O_{11} = C_6H_{10}O_5 + C_6H_{12}O_6.$$

The glucose may be removed from the liquid by fermentation, and the levolusan, which is unfermentable, may be obtained by evaporation as an uncrystallizable syrup. By boiling with water or dilute acids, it is converted into a fermentable levorotatory sugar, probably levulose.

4. **Mannitose**, $C_6H_{12}O_6$.—This is the sugar produced, together with mannitic acid, by the oxidation of mannite in contact with platinum black. It may be separated by saturating the liquid with lime, precipitating the cal-

cium mannitate with alcohol, evaporating the filtrate to a syrup, adding alcohol, again filtering, and evaporating to dryness.

Mannitose is syrupy, uncrystallizable, fermentable, inactive to polarized light, and resembles the other glucoses in its chemical reaction.

5. **Galactose**, $C_6H_{12}O_6$, is produced by boiling milk-sugar with dilute acids. It is soluble in water, sparingly soluble in cold alcohol, crystallizes more readily than ordinary glucose; has a dextro-rotatory power of 83·3°; and is very easily fermentable. It resembles dextro-glucose in most of its reactions, but is distinguished from all the four glucoses above described by yielding mucic instead of saccharic acid, when oxidized by nitric acid.

6. **Inosite**, or **Phaseomannite**, $C_6H_{12}O_6$, is a variety of glucose occurring in the muscular substance of the heart and other organs of the animal body, also in green kidney-beans, the unripe fruit of *Phaseolus vulgaris*, and in many other plants. It forms prismatic crystals, resembling gypsum, soluble in water, but insoluble in alcohol and ether. It may be boiled with strong aqueous potash or baryta without alteration or coloration. If this sugar be evaporated with nitric acid nearly to dryness, the residue mixed with a little ammonia and calcium chloride and again evaporated, a beautiful and characteristic rose tint is produced.

Inosite does not ferment with yeast, but in contact with cheese, flesh, or decaying membrane and chalk, it undergoes lactous fermentation, producing lactic, butyric, and carbonic acids.

7. **Sorbin**, or **Sorbite**, $C_6H_{12}O_6$, is a crystallizable sugar existing in the juice of ripe mountain-ash berries (*Sorbus aucuparia*). The juice, when allowed to stand for some time in open vessels, deposits a brown crystalline matter, which may be obtained in transparent colorless crystals belonging to the trimetric system. This substance is almost insoluble in alcohol, but easily soluble in water, to which it imparts an exceedingly sweet taste. A solution of sorbin, mixed with ammonia and lead acetate, yields a white flocculent precipitate, containing $C_6H_4Pb''O_6$. With *sodium chloride* it forms a compound which crystallizes in cubes.

Sorbin is converted by hot *nitric acid* into oxalic acid. It does not ferment with yeast, but in contact with cheese and chalk, at 40°, it undergoes lactous fermentation, yielding a large quantity of lactic acid, together with alcohol and butyric acid.

8. **Eucalyn**, $C_6H_{12}O_6$, is an unfermentable sugar, separated in the fermentation of melitose (the sugar of the *Eucalyptus* of Tasmania), in consequence of the destruction of a fermentable kind of sugar which, in combination with eucalyn, constitutes melitose:

$$\underset{\text{Melitose.}}{C_{12}H_{22}O_{11}} + OH_2 = 2CO_2 + \underset{\text{Alcohol.}}{2C_2H_6O} + \underset{\text{Eucalyn.}}{C_6H_{12}O_6}$$

On evaporating the liquid, the eucalyn remains as an uncrystallizable syrup, having a specific rotatory power of + 50° nearly. It is not rendered fermentable by the action of sulphuric acid.

GLUCOSIDES.

When ordinary glucose is heated to 100°–120° for fifty or sixty hours with acetic, butyric, stearic, benzoic, and other organic acids, the two unite, with elimination of water, and compound ethers called glucosides

are formed, analogous to the mannitanides. A number of these artificial glucosides have been prepared by Berthelot, who regards them as derivatives of *glucosan*, $C_6H_{10}O_5$, because when heated with alkalies they yield glucosan, not glucose. Thus, there is a glucoso-butyric ether to which Berthelot assigns the formula $C_6H_8(C_4H_7O)_2O_5$, and an acetic ether, which he regards as hexaceto-glucosan, $C_6H_4(C_2H_3O)_6O_5$; but they are merely oily liquids, which are very difficult to obtain pure, and therefore their analyses are not much to be depended on.

A considerable number of bodies of similar constitution exist ready-formed in plants, many of them constituting the bitter principles of the vegetable kingdom. None of these natural glucosides have been produced artificially, but they are all resolved by boiling with dilute acids into glucose and some other compound. We shall describe some of the most important of these bodies.

Aesculin, $C_{21}H_{24}O_{13}$, is a crystalline fluorescent substance obtained from the bark of the horse-chestnut and other trees of the genera *Aesculus* and *Pavia*. It has a bitter taste, is slightly soluble in water and alcohol, more soluble in the same liquids at the boiling heat, nearly insoluble in ether. It is colored red by chlorine. By boiling with hydrochloric or dilute sulphuric acid, it is resolved into glucose and a bitter crystalline substance called *æsculetin:*

$$\underset{\text{Aesculin.}}{C_{21}H_{24}O_{13}} + 3OH_2 = \underset{\text{Glucose.}}{2C_6H_{12}O_6} + \underset{\text{Æsculetin.}}{C_9H_6O_4}$$

The aqueous solution of aesculin is highly fluorescent,* the reflected light being of a sky-blue color. Nearly the same fluorescent tint is exhibited by an infusion of horse-chestnut bark. The color of the latter is, however, slightly modified by the presence of another substance, *paviin*, which exhibits a blue-green fluorescence: it may be separated from aesculin by its greater solubility in ether. Aesculin and paviin appear to exist together in the barks of all species of *Aesculus* and *Pavia*,—aesculin being more abundant in the former, and paviin in the latter.

Amygdalin, $C_{20}H_{27}NO_{11} . 3OH_2$, is a crystalline body existing in bitter almonds, the leaves of the cherry-laurel (*Cerasus laurocerasus*), and many other plants which by distillation yield hydrocyanic acid and bitter-almond oil. These compounds do not exist ready-formed in the plants, but are produced by the decomposition of amygdalin under the influence of emulsin or synaptase, a nitrogenized ferment likewise existing in the plant. The decomposition is expressed by the equation—

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + 2OH_2 = \underset{\substack{\text{Bitter-}\\\text{almond}\\\text{oil.}}}{C_7H_6O} + \underset{\substack{\text{Hydro-}\\\text{cyanic}\\\text{acid.}}}{CNH} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

To prepare amygdalin, the paste of bitter-almonds, from which the fixed oil has been expressed, is exhausted with boiling alcohol, which coagulates the synaptase, renders it inactive, and dissolves out the amygdalin. The alcoholic liquid is distilled in a water-bath, and the syrupy residue is diluted with water, mixed with a little yeast, and set in a warm place to ferment: a portion of sugar, present in the almonds, is thus destroyed. The filtered liquid is then evaporated to a syrup in a water-bath, and mixed with alcohol, which throws down the amygdalin as a white crystalline powder; the latter is collected on a cloth filter, pressed, redissolved in boiling alcohol, and left to cool. It separates in small crystal-

* See Light, p. 91.

line plates of pearly whiteness, which are inodorous and nearly tasteless: it is decomposed by heat, leaving a bulky coal, and diffusing the odor of the hawthorn. In water, both hot and cold, amygdalin is nearly insoluble; a hot saturated solution deposits, on cooling, brilliant prismatic crystals, which contain water. In cold alcohol it dissolves with great difficulty. Heated with dilute nitric acid, or a mixture of dilute sulphuric acid and manganese dioxide, it is resolved into ammonia, bitter-almond oil, benzoic acid, formic acid, and carbonic acid; with potassium permanganate, it yields a mixture of potassium cyanate and benzoate.

Synaptase has never been obtained in a state of purity: it is described as a yellowish-white, opaque, brittle mass, very soluble in water, and coagulable, like albumin, by heat, in which case it loses its specific property. In solution it very soon becomes turbid, and putrefies. The decomposition of amygdalin under the influence of this body may be exhibited by dissolving a portion in a large quantity of water, and adding a little emulsion of sweet almonds: the odor of the volatile oil immediately becomes apparent, and the liquor, on distillation, yields hydrocyanic acid.

Chitin, $C_9H_{15}NO_6$, is the substance which forms the elytra and integuments of insects and the carapaces of crustaceans. It is best prepared by boiling the wing-cases of cockchafers with water, alcohol, ether, acetic acid, and alkalies in succession, as long as anything is dissolved out by each. According to Städeler,* it is resolved by boiling with dilute acids into glucose and lactamide:

$$\underset{\text{Chitin.}}{C_9H_{15}NO_6} + 2OH_2 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Lactamide.}}{C_3H_7NO_2}$$

Gallotannic Acid, $C_{27}H_{22}O_{17}$, the acid contained in the gall-nuts of *Quercus infectoria* and other species of oaks, and of certain species of sumach, is a glucoside, resolved by the action of acids into glucose and gallic acid:

$$\underset{\text{Gallotannic acid.}}{C_{27}H_{22}O_{17}} + 4OH_2 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + 3\underset{\text{Gallic acid.}}{C_7H_6O_5}$$

It will be described in connection with gallic acid. (See the chapter on Acids.)

Glycyrrhizin, $C_{24}H_{36}O_9$; Liquorice-Sugar.—The root of the common liquorice yields a large quantity of a peculiar sweet substance, which is soluble in water, but refuses to crystallize: it cannot be made to ferment. Glycyrrhizin forms difficultly soluble compounds with acids; it is precipitated from its solution by lead, calcium, and barium salts, the precipitate consisting of glycyrrhizin in combination with the base. According to Gorup Besanez, glycyrrhizin when boiled with dilute acids, splits into a resinous body called glycyrretin, and glucose.

$$\underset{\text{Glycyrrhizin.}}{C_{24}H_{36}O_9} + OH_2 = \underset{\text{Glycyrretin.}}{C_{18}H_{26}O_4} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

Myronic Acid, $C_{10}H_{19}NS_2O_{10}$, an acid existing as a potassium salt in the seed of black mustard, is resolved by the action of *myrosin*, an albuminous ferment likewise contained in the seeds, into volatile oil of mustard (allyl sulphocyanate), glucose and sulphuric acid:

$$\underset{\substack{\text{Potassium}\\\text{myronate.}}}{C_{10}H_{18}KNS_2O_{10}} = \underset{\substack{\text{Allyl}\\\text{sulpho-}\\\text{cyanate.}}}{C_3H_5CNS} + \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\substack{\text{Acid}\\\text{potassium}\\\text{sulphate.}}}{SO_4HK}$$

* Ann. Ch. Pharm. cxi. 21.

PHLORIZIN, $C_{21}H_{24}O_{10}.2OH_2$.—This is a substance bearing a great likeness to salicin, found in the root-bark of the apple and cherry-tree, and extracted by boiling alcohol. It forms fine, colorless, silky needles, soluble in 1000 parts of cold water, but freely dissolved by that liquid when hot: it is also soluble without difficulty in alcohol. Dilute acids convert phlorizin into glucose and a crystallizable sweet substance called *phloretin:*

$$\underset{\text{Phlorizin.}}{C_{21}H_{24}O_{10}} + OH_2 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Phloretin.}}{C_{15}H_{14}O_5}$$

Phlorizin, fused with potash, yields *phloretic acid*, $C_9H_{10}O_3$, a beautifully crystalline acid, homologous with salicylic and anisic acids.

QUERCITRIN is a crystallizable yellow coloring matter occurring in quercitron bark, the bark of *Quercus infectoria*, whence it is extracted by boiling with water. Its composition has been variously stated; indeed it is by no means certain that the so-called quercitrins examined by different chemists were really identical substances. According to Hlasiwetz and Pfaundler * it contains $C_{33}H_{30}O_{17}$, and is resolved by boiling with dilute acids into another yellow crystalline body called *quercetin*, and isodulcite (p. 000):

$$\underset{\text{Quercitrin.}}{C_{33}H_{30}O_{17}} + OH_2 = \underset{\text{Quercetin.}}{C_{27}H_{18}O_{12}} + \underset{\text{Isodulcite.}}{C_6H_{14}O_6}$$

SALICIN, $C_{13}H_{18}O_7$, is a crystallizable bitter substance contained in the leaves and young bark of the poplar, willow, and several other trees. It may be prepared by exhausting the bark with boiling water, concentrating the solution to a small bulk, digesting the liquid with powdered lead oxide, and then, after freeing the solution from lead by a stream of sulphuretted hydrogen gas, evaporating till the salicin crystallizes out on cooling. It is purified by treatment with animal charcoal and re-crystallization.

Salicin forms small, white, silky needles, having an intensely bitter taste, but no alkaline reaction. It melts and decomposes by heat, burning with a bright flame, and leaving a residue of charcoal. It is soluble in 5·6 parts of cold water, and in a much smaller quantity when boiling hot. Oil of vitriol colors it deep red.

When distilled with a mixture of potassium bichromate and sulphuric acid, it yields, among other products, a yellow, sweet-scented oil, called *salicylol*, having the composition, $C_7H_6O_2$, and identical with the volatile oil distilled from the flowers of the *Spiræa ulmaria*, or common meadow-sweet.

Salicin, under the influence of the emulsin or synaptase of sweet almonds, is resolved into glucose and *saligenin:*

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + OH_2 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Saligenin.}}{C_7H_8H_2}$$

Saligenin forms colorless, nacreous scales, freely soluble in water, alcohol, and ether. It melts at 82°, and decomposes at a higher temperature. Dilute acids at boiling heat convert it into *saliretin*, C_7H_6O, a resinous substance differing from saligenin by the elements of water. The same substance is produced directly from salicin by boiling with dilute acids. Many oxidizing agents, as chromic acid and silver oxide, convert saligenin into salicylol; even platinum black produces this effect. Its aqueous solution gives a deep indigo-blue color with ferric salts.

Salicin yields, with *chlorine*, substitution-products which are decomposed by synaptase in the same manner as salicin itself, yielding chlorosaligenin, $C_7H_7ClO_2$, and dichlorosaligenin, $C_7H_6Cl_2O_2$. Dilute *nitric acid* converts sali-

* Ann. Ch. Pharm. cxxvii. 362.

cin into helicin, helicoïdin, and anilotic acid. With strong nitric acid, at a high temperature, nitrosalicylic acid, $C_7H_5(NO_2)O_3$, is produced.

Populin, $C_{20}H_{22}O_8$, is a substance resembling salicin in appearance and solubility, but having a penetrating sweet taste. It is found accompanying salicin in the bark and leaves of the aspen. It has the composition of benzoyl-salicin, $C_{13}H_{17}(C_7H_5O)O_7$, and when heated with dilute acids is resolved into benzoic acid, and the products of decomposition of salicin, namely, saliretin and glucose:

$$\underset{\text{Populin.}}{C_{13}H_{17}(C_7H_5O)O_7} + OH_2 = \underset{\text{Benzoic acid.}}{C_7H_6O_2} + \underset{\text{Saliretin.}}{C_7H_6O} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

With potassium bichromate and sulphuric acid, populin yields a considerable quantity of salicylol.

Helicin, $C_{13}H_{16}O_7$, is a white, crystalline, slightly bitter substance, produced by the action of very dilute nitric acid upon salicin:

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + O = OH_2 + \underset{\text{Helicin.}}{C_{13}H_{16}O_7}$$

It is slightly soluble in cold, freely soluble in boiling water, and is resolved by the action of synaptase, or of acids or alkalies at the boiling heat, into glucose and salicylol:

$$\underset{\text{Helicin.}}{C_{13}H_{16}O_7} + OH_3 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Salicylol.}}{C_7H_6O_2}$$

Benzohelicin, $C_{24}H_{20}O_8$, or $C_{13}H_{15}(C_7H_5O)O_7$, produced by the action of dilute nitric acid on benzo-salicin, is resolved in like manner into benzoic acid, salicylol, and glucose:

$$\underset{\text{Benzo-helicin.}}{C_{20}H_{20}O_8} + 2OH_2 = \underset{\text{Benzoic acid.}}{C_7H_6O_2} + \underset{\text{Salicylol.}}{C_7H_6O_2} + \underset{\text{Glucose.}}{C_6H_{12}O_6}$$

Solanine is a crystalline base occurring in various plants of the solanaceous order, especially in the flower-stalks and berries of the woody nightshade (*Solanum dulcamara*), and in the shoots or germs thrown out by potatoes kept in cellars during the winter; it may be extracted from these shoots by water containing a little sulphuric acid. It probably contains $C_{43}H_{71}NO_{16}$, and is resolved by boiling with dilute acids into glucose and *solanidine*, which is also a basic compound crystallizing from alcohol in long needles:

$$\underset{\text{Solanine.}}{C_{43}H_{71}NO_{16}} + 3OH_2 = 3C_6H_{12}O_6 + \underset{\text{Solanidine.}}{C_{25}H_{41}NO}$$

Thujin, $C_{20}H_{22}O_{12}$, is a glucoside occurring in the green parts of the American Arbor Vitæ (*Thuja occidentalis*). It forms shining, lemon-yellow, microscopic crystals, having an astringent taste, and soluble in alcohol. When heated in alcoholic solution with hydrochloric or dilute sulphuric acid, it is resolved into glucose and *thujetin*, $C_{28}H_{28}O_{16}$:

$$2C_{20}H_{22}O_{12} + 4OH_2 = 2C_6H_{12}O_6 + C_{28}H_{28}O_{16}.$$

When heated for a short time only with hydrochloric acid, it yields also another substance called *thujenin*, containing $C_{28}H_{24}O_{14}$, or two molecules of water less than thujetin. Thujin dissolves in baryta water, forming a yellow solution, which when heated deposits an orange-yellow precipitate of *thujetic acid*, $C_{28}H_{22}O_{13}$, while glucose remains dissolved:

$$2C_{20}H_{22}O_{12} + OH_2 = 2C_6H_{12}O_6 + C_{28}H_{22}O_{13}.$$

All these compounds are crystalline.

Xanthorhamnin, $C_{23}H_{28}O_{14}$, a crystallizable yellow coloring matter obtained from Persian or Turkey berries, the seeds of several species of *Rhamnus*, is resolved by boiling with dilute acids, into glucose and *rhamnetin*, $C_{11}H_{10}O_5$, which is also a yellow crystalline substance:

$$C_{23}H_{28}O_{14} + 3OH_2 = 2C_6H_{12}O_6 + C_{11}H_{10}O_5.$$

According to some authorities, xanthorhamnin is identical with quercitrin, and rhamnetin with quercetin.

There are a few compounds which, when treated with dilute acids, split up similarly to the glucosides, but yield saccharine substances differing in composition from glucose. Thus phloretin, as already observed, is resolved into phloretic acid, and phloroglucin, $C_6H_6O_3$ (p. 570), which differs from glucose by $3OH_2$. Quercitrin yields quercetin and isodulcite, $C_6H_{14}O_6$, containing two atoms of hydrogen more than glucose; and *indican*, $C_{26}H_{31}NO_{17}$, yields *indiglucin*, $C_6H_{10}O_6$, containing two atoms of hydrogen less than glucose.

Indican is a colorless substance existing in woad (*Isatis tinctoria*), and probably in most other plants which yield indigo-blue. It likewise occurs in human urine, both healthy and diseased, and when present in considerable quantity, causes the urine, after spontaneous fermentation or addition of acids, to deposit sometimes indigo-blue, sometimes a brown substance isomeric with it, called indirubin.

Indican is decomposed by dilute acids into indigo-blue (or its isomer, indirubin) and indiglucin:

$C_{26}H_{31}NO_{17}$	+	$2OH_2$	=	C_8H_5NO	+	$3C_6H_{10}O_6$
Indican.				Indigo-blue.		Indiglucin.

In contact with aqueous soda or baryta it is resolved into indiglucin, and a yellow uncrystallizable substance called indicanin:

$C_{26}H_{31}NO_{17}$	+	OH_2	=	$C_6H_{10}O_6$	+	$C_{20}H_{23}NO_{12}$;
Indican.				Indiglucin.		Indicanin.

and indicanin, by boiling with dilute acids, is further resolved into indiglucin and other products.

Indiglucin, $C_6H_{10}O_6$, is a colorless or light-yellow syrup, having a slightly sweet taste, soluble in water and alcohol, but precipitated from the alcoholic solution by ether. It is not fermentable, but turns acid by prolonged contact with yeast. It throws down cuprous oxide from an alkaline cupric solution, metallic silver from an ammoniacal solution of the nitrate, and gold from the trichloride. With basic or neutral lead acetate, on addition of ammonia, it forms a precipitate containing $C_{12}H_{18}Pb''O_{12}.3Pb''O$.

POLYGLUCOSIC ALCOHOLS.

The compounds of this group, including cane-sugar and other bodies more or less resembling it, may be regarded as formed by the combination of two or more molecules of glucose, with elimination of a number of molecules of water, less by one than the number of glucose molecules which enter in the combination:

$2C_6H_{12}O_6$	—	H_2O	=	$C_{12}H_{22}O_{11}$, Diglucosic alcohol.
$3C_6H_{12}O_6$	—	$2H_2O$	=	$C_{18}H_{32}O_{16}$, Triglucosic alcohol.
$nC_6H_{12}O_6$	—	$(n-1)H_2O$	=	$C_{6n}H_{10n+2}O_{2n+1}$.

The only known alcohols of this class are diglucosic alcohols, $C_{12}H_{22}O_{11}$; but starch, cellulose, and other plant-constituents appear to be oxygen ethers, or anhydrides, of polyglucosic alcohols of higher orders.

Cane-sugar or **Saccharose**, $C_{12}H_{22}O_{11}$. — This most useful substance is found in the juice of many of the grasses, in the sap of several forest-trees, in the root of the beet and the mallow, and in several other plants. Most sweet fruits contain cane-sugar, together with inverted sugar (p. 577); some, as walnuts, hazelnuts, almonds, coffee-beans, and St. John's-bread (the fruit of *Ceratonia siliqua*), contain only cane-sugar. Honey and the nectars of flowers contain cane-sugar together with inverted sugar; the sugar in the nectars of cactuses is almost wholly cane-sugar.

Sugar is extracted most easily and in greatest abundance from the sugar-cane (*Saccharum officinarum*), cultivated for the purpose in many tropical countries. The canes are crushed between rollers, and the expressed juice is suffered to flow into a large vessel, where it is slowly heated nearly to its boiling point. A small quantity of slaked lime mixed with water is then added, which occasions the separation of a coagulum consisting chiefly of earthy phosphates, waxy matter, a peculiar albuminous principle, and mechanical impurities. The clear liquid separated from the coagulum is rapidly evaporated in open pans, heated by a strong fire made with the crushed canes of the preceding year, which have been dried in the sun, and preserved for the purpose. When sufficiently concentrated, the syrup is transferred to a shallow vessel, and left to crystallize, during which time it is frequently agitated in order to hasten the change and hinder the formation of large crystals. It is, lastly, drained from the dark uncrystallizable syrup, or *molasses*, and sent into commerce, under the name of *raw* or *Muscovado* sugar. The refining of this crude product is effected by redissolving it in water, adding a quantity of albumen in the shape of serum of blood or white of egg, and sometimes a little lime-water, and heating the whole to the boiling point: the albumen coagulates, and forms a kind of network of fibres, which enclose and separate from the liquid all mechanically suspended impurities. The solution is decolorized by filtration through animal charcoal, evaporated to the crystallizing point, and put into conical earthen moulds, where it solidifies, after some time, to a confusedly crystalline mass, which is drained, washed with a little clean syrup, and dried in a stove: the product is ordinary *loaf-sugar*. When the crystallization is allowed to take place quietly and slowly, *sugar-candy* results, the crystals under these circumstances acquiring large volume and regular form. The evaporation of the decolorized syrup is best conducted in strong close boilers exhausted of air; the boiling point of the syrup is reduced in consequence from 110° C. (230° F.) to 65·5° C. (150° F.), or below, and the injurious action of the heat upon the sugar is in great measure prevented. Indeed, the production of molasses in the rude colonial manufacture is chiefly the result of the high and long-continued heat applied to the cane-juice, and might be almost entirely prevented by the use of vacuum-pans, the product of sugar being thereby greatly increased in quantity, and so far improved in quality as to become almost equal to the refined article.

In many parts of the continent of Europe, sugar is manufactured on a large scale from beet-root, which contains about 8 per cent. of that substance. The process is far more complicated and troublesome than that just described, and the raw product much inferior. When refined, however, it is scarcely to be distinguished from the preceding. The inhabitants of the Western States of America prepare sugar in considerable quantity from the sap of the sugar-maple, *Acer saccharinum*, which is comemon in those parts. The tree is tapped in the spring by boring a hole a

little way into the wood, and inserting a small spout to convey the liquid into a vessel placed for its reception. This is boiled down in an iron pot, and furnishes a coarse sugar, which is almost wholly employed for domestic purposes, but little finding its way into commerce.

Pure sugar slowly separates from a strong solution in large, transparent, colorless crystals, having the figure of a modified monoclinic prism. The crystals have a specific gravity of 1·6, and are unchangeable in the air. Sugar has a pure, sweet taste, is very soluble in water, requiring for solution only one-third of its weight in the cold, and is also dissolved by alcohol, but less easily. When moderately heated it melts, and solidifies on cooling to a glassy amorphous mass, familiar as *barley-sugar*.

1. Cane-sugar, heated a little above 160° C. (320° F.), is converted, without loss of weight, into a mixture of dextro-glucose and levolusan (p. 577):

$$C_{12}H_{22}O_{11} = C_6H_{12}O_6 + C_6H_{10}O_5.$$

At a higher temperature, water is given off, the dextro-glucose being probably converted into glucosan (p. 579): afterward, at about 210° C. (410° F.), more water goes off, and a brown substance called *caramel* remains, consisting of a mixture of several compounds, all formed from sugar by elimination of water. At a still higher temperature, an inflammable gaseous mixture is given off, consisting of carbon monoxide, marsh-gas, and carbon dioxide; a distillate is obtained, consisting of brown oils, acetic acid, acetone, and aldehyde; and a considerable quantity of charcoal remains behind. The brown oils contain a small quantity of *furfurol*, and a bitter substance called *assamar*.

2. By prolonged boiling with *water*, cane-sugar is converted into *inverted sugar*. This transformation is accelerated by the presence of acids, and apparently also of certain salts. Different acids act with various degrees of rapidity—mineral more quickly than organic acids, sulphuric acid most quickly of all. When sugar is boiled even with very dilute acids, especially if the boiling be long continued, a number of brown amorphous products are formed, called *ulmin, ulmic acid,** &c.; if the air has access to the liquid, formic acid is likewise produced. Concentrated hydrochloric acid decomposes sugar very quickly.

Strong sulphuric acid decomposes dry sugar when heated, and a concentrated solution, even at ordinary temperatures, with copious evolution of sulphurous oxide, and formation of a large quantity of black carbonaceous matter. By this reaction cane-sugar may be distinguished from glucose.

3. Cane-sugar is very easily oxidized. It reduces silver- and mercury-salts when heated with them, and precipitates gold from the chloride. Pure cupric hydrate is but slowly reduced by it, even at the boiling heat; in presence of alkali, however, a blue solution is formed, and on boiling the liquid, cuprous oxide is slowly precipitated (p. 674). Cane-sugar takes fire when triturated with 8 parts of lead dioxide, and forms with potassium chlorate a mixture which detonates on percussion, and burns vividly when a drop of oil of vitriol is let fall upon it. Distilled with a mixture of sulphuric acid and manganese dioxide, it yields formic acid. Heated with dilute nitric acid, it yields saccharic and oxalic acids. 1 part sugar mixed with 3 parts nitric acid, of specific gravity 1·25 to 1 30, and heated to 50° C. (122° F.), is wholly converted into saccharic acid:

* Under the names *ulmin* and *ulmic acid* have been confounded a number of brown or black uncrystallizable substances produced by the action of powerful chemical agents upon sugar, lignin, &c., or generated by the putrefactive decay of vegetable fibre. Common garden mould, for example, treated with dilute, boiling solution of caustic potassa, yields a deep-brown solution, from which acids precipitate a flocculent, brown substance, having but a slight degree of solubility in water. This is generally called *ulmic* or *humic* acid, and its origin ascribed to the reaction of the alkali on the *ulmin* or *humus* of the soil. It is known that these bodies differ exceedingly in composition: they are too indefinite to admit of ready investigation.

$$\underset{\text{Sugar.}}{C_{12}H_{22}O_{11}} + O_6 = \underset{\text{Saccharic acid.}}{2C_6H_{10}O_8} \quad OH_2$$

At the boiling heat, the product consists chiefly of oxalic acid. Very strong nitric acid, or a mixture of strong nitric and sulphuric acids, converts sugar into *nitrosaccharose*, probably $C_{12}H_{18}(NO_2)_4O_{11}$. Sugar is likewise oxidized by chloride of lime, but the products have not been examined.

4. Cane-sugar does not turn brown when triturated with alkalies, a character by which it is distinguished from glucose: it combines with them, however, forming compounds called *sucrates*. By boiling with potash-lye it is decomposed, but much more slowly than the glucoses.

Potassium- and *Sodium-compounds* of cane-sugar, $C_{12}H_{21}KO_{11}$ and $C_{12}H_{21}NaO_{11}$, are formed, as gelatinous precipitates, on mixing an alcoholic solution of cane-sugar with potash- or soda-lye.

A *barium-compound*, $C_{12}H_{20}Ba''O_{11} . H_2O$, or $C_{12}H_{22}O_{11} . Ba''O$, is obtained, as a crystalline precipitate, on adding hydrate or sulphide of barium to an aqueous solution of sugar. It may be crystallized from boiling water, but is insoluble in alcohol.

Calcium-compounds.—Lime dissolves in sugar-water much more readily than in pure water. The solution has a bitter taste, and is completely but slowly precipitated by carbonic acid. There are three or four of these compounds, which may be approximately represented by the following formulæ:

1. $C_{12}H_{22}O_{11} . Ca''O$.
2. $2C_{12}H_{22}O_{11} . 3Ca''O$ (?)
3. $C_{12}H_{22}O_{11} . 2Ca''O . 2H_2O$.
4. $C_{12}H_{22}O_{11} . 3Ca''O$.

Magnesia and *lead oxide* are also dissolved by sugar-water. A crystalline lead-compound, $C_{12}H_{18}Pb''_2O_{11}$, is precipitated on mixing sugar-water with neutral lead-acetate and ammonia.

Sugar also forms, with *sodium chloride*, a crystalline compound containing $C_{12}H_{22}O_{11} . NaCl$.

Cane-sugar is not directly fermentable, but when its dilute aqueous solution is mixed with yeast, and exposed to a warm atmosphere, it is first resolved into a mixture of dextrose and levulose (p. 577), which then enter into fermentation, yielding alcohol and carbon dioxide.

Parasaccharose, $C_{12}H_{22}O_{11}$.—This is an isomer of cane-sugar, produced, according to Jodin,* by spontaneous fermentation. An aqueous solution of cane-sugar containing ammonium phosphate left to itself for three months in summer, yielded, under circumstances not further specified, a crystallizable sugar, isomeric with saccharose, together with an amorphous sugar having the composition of a glucose, both dextro-rotatory. Parasaccharose is very soluble in water, nearly insoluble in alcohol of 90 per cent. Its specific rotatory power at 10° = + 108°, appearing to increase a little with rise of temperature. It does not melt at 100°, but becomes colored, and appears to decompose. It reduces an alkaline cupric solution, but only half as strongly as dextro-glucose. It is not perceptibly altered by dilute sulphuric acid, even at 100°; hydrochloric acid weakens its rotatory power, turns the solution brown, and heightens its reducing power for cupric oxide.

Melitose, $C_{12}H_{22}O_{11}$.—A kind of sugar obtained from the manna which falls in opaque drops from various species of *Eucalyptus* growing in Tasmania. It is extracted by water, and crystallizes in extremely thin interlaced needles, having a slightly saccharine taste.

The crystals of melitose are hydrated, containing $C_{12}H_{22}O_{11} . 3OH_2$. They give off 2 atoms water at 100°, and become anhydrous at 130° C. (266° F.).

* Comptes Rendus, tom. liii. p. 1252; liv. 720.

They dissolve in 9 parts of cold water, very easily in boiling water, and dissolve also in boiling alcohol more freely than mannite. The alcoholic solution yields small but well-developed crystals. The aqueous solution turns the plane of polarization to the right: for the transition tint $[a] = + 102°$.

Melitose, heated with dilute sulphuric acid, is resolved into a fermentable sugar (probably dextroglucose), and non-fermentable eucalyn (p. 578). Melitose ferments in contact with yeast, but is resolved, in the first instance, into glucose and eucalyn. It does not reduce an alkaline cupric solution, and is not altered by boiling with dilute alkalies or with baryta-water. It is oxidized by nitric acid, yielding a certain quantity of mucic acid, together with a large quantity of oxalic acid.

Melezitose, $C_{12}H_{22}O_{11}$.—This variety of sugar is found in the so-called manna of Briançon, which exudes from the young shoots of the larch (*Larix Europæa*). The manna is exhausted with alcohol, which, when evaporated, yields melezitose in very small, hard, shining efflorescent crystals, which give off 4 per cent. of water when heated, melt below 140° without further alteration, forming a liquid which solidifies to a glass on cooling. Melezitose is dextro-rotatory; $[a] = + 94{\cdot}1°$. It dissolves easily in water, is nearly insoluble in cold, slightly soluble in boiling alcohol.

Melezitose decomposes at about 200° C. (392° F.). It is carbonized by cold strong sulphuric acid, quickly turns brown with boiling hydrochloric acid, and forms oxalic acid with nitric acid. By an hour's boiling with dilute sulphuric acid, it is converted into glucose. In contact with yeast it passes slowly, or sometimes not at all, into vinous fermentation. It is not altered at 100° by aqueous alkalies, and scarcely by potassio-cupric tartrate.

Trehalose, $C_{12}H_{22}O_{11} . 2OH_2$, is obtained from *Trehala manna*, the produce of a species of Echinops growing in the East, by extraction with boiling alcohol. It forms shining rhombic crystals, containing $C_{12}H_{22}O_{11} . 2OH_2$, which melt when quickly heated to 109° C. (228° F.); but if slowly heated give off their water even below 100°. It has a strongly saccharine taste, dissolves easily in water and in boiling alcohol, but is insoluble in ether. The aqueous solution is dextro-rotatory; $[a] = + 199°$.

By several hours' boiling with dilute sulphuric acid, it is converted into dextroglucose. With strong nitric acid it forms a detonating nitro-compound; heated with dilute nitric acid it yields oxalic acid. In contact with yeast it passes slowly and imperfectly into alcoholic fermentation. It is not altered by boiling with alkalies, and does not reduce cuprous oxide from alkaline cupric solutions. Heated with acetic or butyric acid, it yields compounds not distinguishable from those which are formed in like manner from dextroglucose (p. 577).

Mycose, $C_{12}H_{22}O_{11} . 2OH_2$, is a kind of sugar very much like trehalose, obtained from ergot of rye by precipitating the aqueous extract of the fungus with basic lead acetate, removing the lead from the filtrate by sulph-hydric acid, evaporating to a syrup, and leaving the liquid to crystallize. It differs from trehalose only in possessing a somewhat feebler rotatory power; $[a] = + 192{\cdot}5°$, and in not being completely dehydrated at 100°.

Milk-sugar, Lactin, or Lactose, $C_{12}H_{22}O_{11} . OH_2$.—This kind of sugar is an important constituent of milk; it is obtained in large quantities by evaporating *whey* to a syrupy state, and purifying the lactose, which slowly crystallizes out, with animal charcoal. It forms white, translucent, four-sided, trimetric prisms, of great hardness. It is slow and difficult of solution in cold water, requiring for that purpose 5 or 6 times its weight: it

has a faint, sweet taste, and in the solid state feels gritty between the teeth. When heated, it loses water, and at a high temperature blackens and decomposes. Milk-sugar combines with bases, forming compounds which have an alkaline reaction, and are easily decomposed. Dilute acids convert it into galactose (p. 578).

Milk-sugar, when distilled with oxidizing mixtures, such as sulphuric acid and manganese dioxide, yields formic acid. With nitric acid, it forms mucic, saccharic, tartaric, and a small quantity of racemic acid, and finally oxalic acid. Very strong nitric acid, or a mixture of nitric and sulphuric acids, converts milk-sugar into a crystalline substitution-product called *nitro-lactin*.

Milk-sugar is not brought immediately by yeast into the state of alcoholic fermentation; but when it is left for some time in contact with yeast, fermentation gradually sets in. When cheese or gluten is used as the ferment, the milk-sugar is converted into lactic acid. Alcohol is, however, always formed at the same time, especially if no chalk is added to neutralize the acid as it forms; the quantity of alcohol formed is greater also as the solution is more dilute.

Gum. — *Gum-arabic*, which is the produce of several species of acacia, may be taken as the most perfect type of this class of bodies. In its purest and finest condition, it forms white or slightly yellowish irregular masses, which are destitute of crystalline structure, and break with a smooth conchoïdal fracture. It is soluble in cold water, forming a viscid, adhesive, tasteless solution, from which the pure soluble gummy principle, or *arabin*, is precipitated by alcohol, and by basic lead acetate, but not by the neutral acetate. Arabin is composed of $C_{12}H_{22}O_{11}$, and is consequently isomeric with cane-sugar.

Mucilage, so abundant in linseed, in the roots of the mallow, in *salep*, the fleshy root of *Orchis mascula*, and in other plants, differs in some respects from gum-arabic, although it agrees in the property of dissolving in cold water. The solution is less transparent than that of gum, and is precipitated by neutral lead acetate. *Gum-tragacanth* is chiefly composed of a kind of mucilage to which the name *bassorin* has been given; it refuses to dissolve in water, merely softening and assuming a gelatinous aspect. It is dissoved by caustic alcali. *Cerasin* is the insoluble portion of the gum of the cherry-tree; it resembles bassorin. The composition of these various substances has been carefully examined by Schmidt, who finds that it closely agrees with that of starch. Mucilage invariably contains hydrogen and oxygen in the proportion in which they form water, and when treated with acid, yields glucose.

Pectin, or the jelly of fruits, is, in its physical properties, closely allied to the foregoing bodies. It may be extracted from various vegetable juices by precipitation with alcohol. It forms when moist a transparent jelly, which is soluble in water, tasteless, and dries up to a translucent mass. It is to this substance that the firm consistence of currant and other fruit-jellies is ascribed. According to Frémy, the composition of pectin is $C_{32}H_{48}O_{32}$. By ebullition with water and with dilute acids it is changed into two isomeric modifications, called *parapectin* and *metapectin*. In contact with bases, these three substances are converted into *pectic acid*, $C_{16}H_{22}C_{15}$ (?), which closely resembles pectin, except that it possesses feeble acid properties, and is insoluble in water. By long boiling with caustic alkali, a further change is produced, and *metapectic acid*, $C_{24}H_{32}O_{27}$ (?), is formed, which does not gelatinize. The metallic pectates and metapectates are uncrystallizable. Much doubt still exists respecting the composition of the various bodies of the pectin group; but from the analyses hitherto made, they do not appear to contain hydrogen and oxygen in the proportion to form water, and therefore scarcely belong to the sugar and starch group.

OXYGEN-ETHERS, OR ANHYDRIDES, OF THE POLYGLUCOSIC ALCOHOLS.

These compounds, which are important constituents of the vegetable organism, may be derived from glucose and the polyglucosic alcohols by abstraction of a molecule of water:

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} - H_2O = C_6H_{10}O_5,$$

$$\underset{\text{Diglucosic alcohol.}}{C_{12}H_{22}O_{11}} - H_2O = C_{12}H_{20}O_{10}, \text{ or } 2C_6H_{10}O_5,$$

$$\underset{\text{Triglucosic alcohol.}}{C_{18}H_{32}O_{16}} - H_2O = C_{18}H_{30}O_{15}, \text{ or } 3C_6H_{10}O_5,$$

$$\vdots$$

$$C_{6n}H_{10n+2}O_{5n+1} - H_2O = C_{6n}H_{10n}O_{5n}, \text{ or } nC_6H_{10}O_5.$$

All these bodies are therefore isomeric or polymeric one with the other. Their compounds with metallic oxides, &c., have not been sufficiently investigated to fix their exact molecular weight, or to determine in each case the value of n; but from the mode of conversion of starch into glucose, and the constitution of certain substitution-products obtained by the action of nitric acid on cellulose, it appears most probable that in these bodies $n=3$.

Starch, $nC_6H_{10}O_5$, probably $C_{18}H_{30}O_{15}$, also called *Fecula* and *Amidine*.— This is one of the most important and widely diffused of the vegetable proximate principles, being found to a greater or less extent in every plant. It is most abundant in certain roots and tubers, and in soft stems: seeds often contain it in large quantity. From these sources the starch can be obtained by rasping or grinding the vegetable structure to pulp, and washing the mass upon a sieve, by which the torn cellular tissue is retained, while the starch passes through with the liquid, and eventually settles down from the latter as a soft, white, insoluble powder, which may be washed with cold water, and dried at a very gentle heat. Potatoes treated in this manner yield a large proportion of starch. Starch from grain may be prepared in the same manner, by mixing the meal with water to a paste, and washing the mass upon a sieve: a nearly white, insoluble substance called *gluten* is then left, containing a large proportion of nitrogen. The gluten of wheat-flour is extremely tenacious and elastic. The value of meal as an article of food greatly depends upon this substance. Starch from grain is commonly manufactured on the large scale by steeping the material in water for a considerable time, when the lactic acid, always developed under such circumstances from the sugar of the seed, disintegrates, and in part dissolves the azotized matter, thereby greatly facilitating the mechanical separation of that which remains. A still more easy and successful process has lately been introduced, in which a very dilute solution of caustic soda, containing about 200 grains of alkali to a gallon of liquid, is employed with the same view. Excellent starch is thus prepared from rice. Starch is insoluble in cold water, as

Fig. 193.

indeed its mode of preparation sufficiently shows: it is equally insoluble in alcohol and other liquids, which do not effect its decomposition. To the naked eye it presents the appearance of a soft, white, and often glistening powder: under the microscope it is seen to be altogether destitute of crystalline structure, but to possess, on the contrary, a kind of organization, being made up of multitudes of little rounded transparent bodies, upon each of which a series of depressed parallel rings, surrounding a central spot or hilum, may often be traced. The starch-granules from different plants vary both in magnitude and form: those from the *Canna coccinea*, or *tous les mois*, and potato being largest; and those from wheat, and the cereals in general, very much smaller. Figure 193 will serve to convey an idea of the appearance of the granules of potato-starch, highly magnified.

When a mixture of starch and water is heated to near the boiling-point of the latter, the granules burst and disappear, producing, if the proportion of starch be considerable, a thick gelatinous mass, very slightly opalescent, from the shreds of fine membrane, the envelope of each separate granule. By the addition of a large quantity of water, this gelatinous starch, or *amidin*, may be so far diluted as to pass in great measure through filter-paper. It is very doubtful, however, how far the substance itself is really soluble in water, at least when cold; it is more likely to be merely suspended in the liquid in the form of a swollen, transparent, and insoluble jelly, of extreme tenuity. Gelatinous starch, exposed in a thin layer to a dry atmosphere, becomes converted into a yellowish, horny substance, like gum, which, when put into water, again softens and swells.

Thin gelatinous starch is precipitated by many of the metallic oxides, as lime, baryta, and lead oxide; also by a large addition of alcohol. *Infusion of galls* throws down a copious yellowish precipitate containing tannic acid, which re-dissolves when the solution is heated. By far the most characteristic reaction, however, is that with free *iodine*, which forms with starch a deep indigo-blue compound, which appears to dissolve in pure water, although it is insoluble in solutions containing free acid or saline matter. The blue liquid has its color destroyed by heat, temporarily if the heat be quickly withdrawn, and permanently if the boiling be long continued, in which case the compound is decomposed and the iodine volatilized. Dry starch, put into iodine-water, acquires a purplish-black color.

The unaltered and the gelatinous starch, in a dried state, have the same empirical formula, $C_6H_{10}O_5$. A compound of starch and lead oxide was found to contain, when dried at 100°, $C_6H_{10}O_5 \cdot PbO$, or $C_{18}H_{30}O_{15} \cdot 3PbO$.

Dextrin.—When gelatinous starch is boiled with a small quantity of dilute sulphuric, hydrochloric, or indeed, almost any acid, it speedily loses its consistency, and becomes thin and limpid, from having suffered conversion into a soluble gum-like substance, called dextrin, on account of its dextro-rotatory action on polarized light. The experiment is most conveniently made with sulphuric acid, which may be afterward withdrawn by saturation with chalk. The liquid filtered from the nearly insoluble gypsum, may then be evaporated to dryness in a water-bath. The result is a gum-like mass, destitute of crystalline structure, soluble in cold water, precipitable from its solution by alcohol, and capable of combining with lead oxide.

When the ebullition with the dilute acid is continued for a considerable time, the dextrin first formed undergoes a further change, and becomes converted into dextro-glucose, which can be thus artificially produced with the greatest facility. The length of time required for this remarkable change depends upon the quantity of acid present; if the latter be very small, it is necessary to continue the boiling many successive hours, re-

placing the water which evaporates. With a larger proportion of acid, the conversion is much more speedy. A mixture of 15 parts of potato-starch, 60 parts water, and 6 parts sulphuric acid, may be kept boiling for about four hours; the liquid neutralized with chalk, filtered, and rapidly evaporated to a small bulk. By digestion with animal charcoal and a second filtration, much of the color will be removed, after which the solution may be boiled down to a thin syrup and left to crystallize: in the course of a few days it solidifies to a mass of glucose. There is another method of preparing this substance from starch which deserves particular notice. Germinating seeds, and buds in the act of development, are found to contain a small quantity of a peculiar azotized substance, called *diastase;* formed at this particular period from the gluten of vegetable albuminous matter. This substance possesses the same curious property of effecting the conversion of starch into dextrin and glucose, and at a much lower temperature than that of ebullition. When a little infusion of malt, or germinated barley, in tepid water, is mixed with a large quantity of thick gelatinous starch, and the whole maintained at about 71°, complete liquefaction takes place in the space of a few minutes from the production of dextrin and glucose. If a greater degree of heat be employed, the diastase is coagulated and rendered insoluble and inactive. Very little is known respecting diastase itself; it seems very much to resemble vegetable albumin, but has never been obtained in a state of purity.

The change of starch or dextrin into sugar, whether produced by the action of dilute acid or by diastase, takes place quite independently of the oxygen of the air, and is unaccompanied by any secondary product. The acid takes no direct part in the reaction; it may, if not volatile, be all withdrawn without loss after the experiment. The whole reaction lies between the starch and the elements of water, a fixation of the latter occurring in the new product, as will be seen on comparing the composition of starch and glucose. Dextrin itself has exactly the same composition as the original starch.

It was formerly supposed that, in the action of acids or of disastase upon starch, the starch is first converted into dextrin by a mere alteration of physical structure, and that the dextrin then takes up the elements of water, and is converted into glucose, this second stage of the process occupying a much longer time than the first; but from recent experiments by Musculus* it appears that both dextrin and glucose are produced at the very commencement of the reaction, and always in the proportion of 1 molecule of glucose to 2 molecules of dextrin, whence it may be inferred that the molecule of starch contains $C_{18}H_{30}O_{15}$, and that it is resolved into glucose and dextrin by taking up a molecule of water:

$$\underset{\text{Starch.}}{C_{18}H_{30}O_{15}} + OH_2 = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Dextrin.}}{2C_6H_{10}O_5}$$

When the conversion is effected by a dilute acid, the dextrin is, after several hours' boiling, completely converted into glucose, which is therefore the sole ultimate product of the reaction. But when diastase is used as the converting agent, the production of glucose goes on only so long as there is any unaltered starch still present, the dextrin undergoing no further alteration.

Dextrin is used in the arts as a substitute for gum; it is sometimes made in the manner above described, but more frequently by heating dry potato-starch to 400° C. (752° F.), by which it acquires a yellowish tint and becomes soluble in cold water. It is sold in this state under the name of *British Gum.*

Starch is an important article of food, especially when associated, as in

* Comptes Rendus, l. 785; liv. 194; Ann. Ch. Phys. [3], lx. 208; [4], vi. 177.

ordinary meal, with albuminous substances. Arrowroot, and the fecula of the *Canna coccinea*, are very pure varieties, employed as articles of diet; arrowroot is obtained from the *Maranta arundinacea*, cultivated in the West Indies; it is with difficulty distinguished from potato-starch. — *Tapioca* is prepared from the root of the *Jatropha manihot*, being thoroughly purified from its poisonous juice. — *Cassava* is the same substance modified while moist by heat. — *Sago* is made from the soft central portion of the stem of a palm; and *salep* from the fleshy root of the *Orchis mascula*.

Starch from Iceland Moss. — The lichen called *Cetraria Islandica*, purified by a little cold solution of potash from a bitter principle, yields, when boiled in water, a slimy and nearly colorless liquid, which gelatinizes on cooling, and dries up to a yellowish amorphous mass, which does not dissolve in cold water, but merely softens and swells. A solution of this substance in warm water is not affected by iodine, although the jelly is rendered blue. It is precipitated by alcohol, lead acetate, and infusion of galls, and is converted into glucose by boiling with dilute sulphuric acid. According to Mulder, it contains $C_6H_{10}O_5$. The jelly from certain *algæ*, as that of Ceylon, and the so-called *Carragheen moss*, closely resembles the above.

Inulin. — This substance, which differs from common starch in some important particulars, is found in the root of *Inula helenium*, *Helianthus tuberosus*, *dahlia*, and several other plants: it may be easily obtained by washing the rasped root on a sieve, and allowing the inulin to settle down from the liquid; or by cutting the root into thin slices, boiling these in water, and filtering while hot; the inulin separates as the solution cools. It is a white, amorphous, tasteless substance, nearly insoluble in cold water, but freely dissolves by the aid of heat; the solution is precipitated by alcohol, but not by acetate of lead or infusion of galls. Iodine colors it brown. Inulin has the same percentage composition as common starch. By boiling with dilute acids, it is completely converted into levulose (p. 577)

Cellulose, $nC_6H_{10}O_5$, probably $C_{18}H_{30}O_{15}$; also called *Lignin*. — This substance constitutes the fundamental material of the structure of plants; it is employed in the organization of cells and vessels of all kinds, and forms a large proportion of the solid parts of every vegetable. It must not be confounded with *ligneous* or *woody tissue*, which is in reality cellulose with other substances superadded, incrusting the walls of the original membranous cells, and conferring stiffness and inflexibility. Thus woody tissue, even when freed as much as possible from coloring matter and resin by repeated boiling with water and alcohol, yields, on analysis, a result indicating an excess of hydrogen above that required to form water with the oxygen, besides traces of nitrogen. Pure cellulose, on the other hand, has the same percentage composition as starch.*

The properties of cellulose may be conveniently studied in fine linen and cotton, which are almost entirely composed of the body in question, the associated vegetable principles having been removed or destroyed by the variety of treatment to which the fibre has been subjected. Pure cellulose is tasteless, insoluble in water and alcohol, and absolutely innutritious: it is not sensibly affected by boiling water, unless it happens to have been derived from a soft or imperfectly developed portion of the plant, in which case it is disintegrated and rendered pulpy. Dilute acids and alkalies exert but little action on lignin, even at a boiling temperature; strong oil of vitriol converts it, in the cold, into a nearly colorless, adhesive substance, which dissolves in water, and presents the characters

* *Dumas*, Chimie appliquée aux Arts, vi. 5.

of dextrin. This curious and interesting experiment may be conveniently made by very slowly adding concentrated sulphuric acid to half its weight of lint, or linen cut into small shreds, taking care to avoid any rise of temperature which would be attended with charring or blackening. The mixing is completed by trituration in a mortar, and the whole left to stand a few hours; after which it is rubbed up with water, warmed, and filtered from a little insoluble matter. The solution may then be neutralized with chalk, and again filtered. The gummy liquid retains lime, partly in the state of sulphate, and partly in combination with sulpholignic acid, an acid composed of the elements of sulphuric acid, in union with those of cellulose. If the liquid, previous to neutralization, be boiled during three or four hours, and the water replaced as it evaporates, the dextrin becomes entirely changed to glucose. Linen rags may, by these means, be made to furnish more than their own weight of that substance. If a piece of unsized paper be dipped for a few seconds into a mixture of 2 volumes of concentrated sulphuric acid and 1 volume of water, and then thoroughly washed with water and dilute ammonia, a substance is obtained which resembles parchment, and has the same composition as cellulose; it occurs in commerce under the name of parchment paper (papyrin). An excellent application of this substance in diffusion experiments is mentioned on page 149.

Cellulose dissolves in an ammoniacal solution of cupric oxide (prepared by dissolving basic cupric carbonate in strong ammonia), from which it is precipitated by acids in colorless flakes.

Cellulose is not colored by iodine.

Xyloïdin and Pyroxylin.—When starch is mixed with nitric acid of specific gravity 1·5, it is converted, without disengagement of gas, into a transparent, colorless jelly, which, when put into water, yields a white, curdy, insoluble substance: this is *xyloïdin*. When dry, it is white and tasteless, insoluble even in boiling water, but freely dissolved by dilute nitric acid, and the solution yields oxalic acid when boiled. Other substances belonging to the same class also yield xyloïdin; paper dipped into the strongest nitric acid, quickly plunged into water, and afterward dried, becomes in great part so changed: it assumes the appearance of parchment, and acquires an extraordinary degree of combustibility.

If pure, finely divided ligneous matter, as cotton-wool, be steeped for a few minutes in a mixture of nitric acid of sp. gr. 1·5 and concentrated sulphuric acid, then squeezed, thoroughly washed, and dried by very gentle heat, it will be found to have increased in weight about 70 per cent., and to have become highly explosive, taking fire at a temperature not much above 149° C. (300° F.), and burning without smoke or residue. This is *pyroxylin*, the *gun-cotton* of Professor Schönbein.

Xyloïdin and pyroxylin are substitution-products consisting of starch and cellulose, in which the hydrogen is more or less replaced by nitryl, NO_2. Xyloïdin consists of $C_6H_9(NO_2)O_5$, or $C_{18}H_{27}(NO_2)_3O_{15}$. Of pyroxylin several varieties are known, distinguished by their different degrees of stability and solubility in alcohol, ether, and other liquids. According to Hadow,* the three principal varieties are:

α.—$C_{18}H_{21}(NO_2)_9O_{15}$, or $C_6H_7(NO_2)_3O_5$, insoluble in a mixture of ether and alcohol, but soluble in ethylic acetate. It is produced by repeated immersion of cotton-wool in a mixture of 2 molecules of nitric acid, NO_3H, 2 molecules of oil of vitriol, SO_4H_2, and three molecules of water.

β.—$C_{18}H_{22}(NO_2)_8O_{15}$, soluble in ether-alcohol, insoluble in glacial acetic

* Chem. Soc. Journal, vii. 201.—A series of elaborate and valuable researches on gun-cotton has recently been published by *Abel* (Proceed. Royal Soc.) xv. 182; Chem. Soc. J. [2], xv. 310.

acid. Produced when the acid mixture contains half a molecule more water than in *α*.

γ.—$O_{18}H_{23}(NO_2)_7O_{15}$ (Gladstone's *cotton-xyloïdin*), soluble in ether and in glacial acetic acid. Produced when the acid mixture contains one molecule more water than in *α*.

The first of these, which consists of *trinitrocellulose*, is the most explosive of the three, and the least liable to spontaneous decomposition. It is the only one adapted for use in gunnery, and is especially distinguished as "gun-cotton." From the experiments of General von Lenk, of the Austrian service, it appears that to insure the uniform production of this particular compound the following precautions are necessary:

1. The cleansing and perfect desiccation of the cotton, previously to its immersion in the mixed acids.—2. The employment of the strongest acids procurable in commerce.—3. The steeping of the cotton in a fresh strong mixture of acids after the first immersion and partial conversion into gun-cotton.—4. The continuance of the steeping for forty-eight hours.—5. The thorough purification of the gun-cotton thus produced from every trace of free acid, by washing the product in a stream of water for several weeks; subsequently a weak solution of potash may be used, but this is not essential.

The solution of the less highly nitrated compounds in alcohol and ether is called *collodion*. This solution, when left to evaporate, dries up quickly to a thin, transparent, adhesive membrane: it is employed with great advantage in surgery as an air-tight covering for wounds and burns. It is also largely used in photography (p. 98).

Glycogen, $n(C_6H_{10}O_5)$, was obtained by Bernard from the liver of several animals (calf or pig) by exhaustion with water and precipitating with boiling alcohol. The precipitate is purified by boiling with dilute potash, repeatedly dissolving in strong acetic acid, and precipitating by alcohol. Glycogen also enters largely into the composition of most of the tissues of the embryo. The muscles of fœtal calves of three to seven months have been found to yield from 20 to 50 per cent. of it.

Glycogen is a white, amorphous, starch-like substance, without odor or taste, yielding an opalescent solution with water, but insoluble in alcohol. It does not reduce an alkaline solution of copper. This substance does not ferment with yeast, but is converted into glucose by boiling with dilute acids, or by contact with diastase, pancreatic juice, saliva, or blood.

ORGANIC ACIDS.

ORGANIC ACIDS, or carbon acids, are derived, as we have several times had occasion to observe, from alcohols, by the substitution of oxygen for an equivalent quantity of hydrogen (O for H_2); in fact they are often produced directly from alcohols by the action of oxidizing agents. Now the formula of an alcohol is derived from that of a hydrocarbon by substitution of one or more equivalents of hydroxyl (OH) for an equal number of hydrogen-atoms, the number of such substitutions determining the atomicity of the alcohol (p. 508), that is to say, the number of its hydrogen-atoms that can be replaced by a monatomic alcohol radical or acid radical, and in some cases by an alkali-metal; in other words, the number of ethers that an alcohol can form with a monatomic alcohol radical is equal to the number of equivalents of hydroxyl contained in its molecules; thus glycerin, which is a triatomic molecule, yields three ethylic ethers:

CH_2OH	$CH_2OC_2H_5$	$CH_2OC_2H_5$	$CH_2OC_2H_5$
$CHOH$	$CHOH$	$CHOH$	$CHOC_2H_5$
CH_2OH	OH_2OH	$CH_2OC_2H_5$	$CH_2OC_2H_5$
Glycerin.	Mono ethylin.	Diethylin.	Triethylin.

The hydrogen thus replaceable, called *typic hydrogen*, is that which is combined with the carbon, not directly, but only through the medium of oxygen.

The number of acids which any alcohol can yield is equal to the number of times that the group or radical, CH_2OH, enters into its molecule; and the passage from the alcohol to the acid consists in the substitution of O for H_2 in this group, or in the conversion of CH_2OH into the acid radical COOH, called *oxatyl*. Thus ethyl alcohol, $\begin{matrix} CH_3 \\ | \\ CH_2OH \end{matrix}$, which is monatomic, can yield but one acid, namely, acetic acid, $\begin{matrix} CH_3 \\ | \\ COOH \end{matrix}$; but ethene alcohol or glycol, which is diatomic, yields two, viz., glycollic and oxalic acids:

CH_2OH	CH_2OH	$COOH$
CH_2OH	$COOH$	$COOH$
Ethene alcohol.	Glycollic acid.	Oxalic acid.

Further observation shows that the *basicity* of an organic acid, that is to say the number of its hydrogen-atoms that can be replaced by metals to form salts, is equal to the number of equivalents of oxatyl contained in it, or, in other words, to the number of hydrogen-molecules (H_2) that have been replaced by oxygen (O), in the immediate neighborhood of hydroxyl (OH), to convert the alcohol into an acid. Thus from propene-glycol, $C_3H_8O_2$, are derived the two diatomic acids, lactic acid, $C_3H_6O_3$, which is monobasic, and malonic acid, $C_3H_4O_4$, which is bibasic:

CH_2OH	CH_2OH	$COOH$
|	|	|
CH_2	CH_2	CH_2
|	|	|
CH_2OH	$COOH$	$COOH$
Propene glycol.	Lactic acid.	Malonic acid.

The atomicity of an acid is the same as that of the alcohol from which it is derived; thus lactic acid, though it contains only one atom of basic hydrogen, and therefore forms only one class of metallic salts, represented by the formula $C_3H_5O_3M$, can form two ethylic ethers, viz., ethyl-lactic acid and diethyl-lactate or ethyl-lactate; thus:

CH_2OH	$CH_2OC_2H_5$	$CH_2OC_2H_5$
|	|	|
CH_2	CH_2	CH_2
|	|	|
$COOH$	$COOH$	$COOC_2H_5$
Lactic acid (monobasic).	Ethyl-lactic acid (monobasic).	Diethylic lactate (neutral).

From these considerations it appears, that monatomic acids must necessarily be monobasic; but diatomic acids may be either monobasic or bibasic; triatomic acids, either monobasic, bibasic, or tribasic; and so on.

Many of the most important acids are derived, in the manner above explained, from actually known alcohols; others, though they have no alcohols actually corresponding to them, are homologous with other acids derived from known alcohols; but there is also a considerable number of acids, especially those formed in the vegetable or animal organism, which cannot be regarded as derivatives of alcohols of any known series; but the number of these unclassified acids will doubtless diminish as their composition and reactions become more thoroughly known.

These acids may also be regarded as compounds of hydroxyl with oxygenated radicals (acid radicals) formed from the corresponding alcohol-radicals by substitution of O for H_2, or as derived from one or more molecules of water (according to their atomicity), by substitution of such radicals for half the hydrogen in the water; *e. g.*,

Type.		
$\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O$	$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O$
Water.	Ethyl alcohol.	Acetic acid.

$\left.\begin{matrix}H\\H\end{matrix}\right\}O$ $\left.\begin{matrix}H\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\(C_3H_6)''\\H\end{matrix}\right\}O$ $\left.\begin{matrix}\\\\H\end{matrix}\right\}O$	$\left.\begin{matrix}H\\(C_3H_4O)''\\H\end{matrix}\right\}O$ $\left.\begin{matrix}\\\\H\end{matrix}\right\}O$	$\left.\begin{matrix}(C_3H_2O_2)''\\H_2\end{matrix}\right\}O_2$
Water (2 mol.)	Propene glycol.	Lactic acid.	Malonic acid.

In these typical formulæ of polyatomic acids, the typic or alcoholic hydrogen (replaceable only by alcoholic or acid radicals), is placed, for distinction, above the acid radical; and the basic hydrogen, replaceable either by metals or alcohol radicals, below.

The acid radicals are denoted by names ending in *yl*, formed from those of the acids themselves; thus, C_2H_3O, the radical of acetic acid, is called *acetyl*; C_3H_4O, is *lactyl*; $C_3H_2O_2$, is *malonyl*, &c.

The replacement of the hydroxyl in an acid by chlorine, bromine, or

iodine, gives rise to acid chlorides, &c.; thus from acetic acid, $C_2H_3O(OH)$, is derived acetic chloride, C_2H_3OCl, &c. The replacement of the hydrogen within the radical (radical hydrogen) by the same elements, or by the radicals, CN, NO_2, NH_2, &c., gives rise to chlorinated, brominated, cyanated, nitrated, and amidated acids (see p. 469). Lastly, the replacement of the *typic* hydrogen by alcohol-radicals gives rise to ethereal salts or compound ethers; and its replacement by acid radicals yields acid oxides or anhydrides (p. 469). The derivatives of each acid will be described in connection with the acid itself.

MONATOMIC ACIDS.

These acids, being derived from monatomic alcohols by substitution of O for H_2, necessarily contain two atoms of oxygen. Each series of hydrocarbons yields a series of monatomic alcohols and a series of monatomic acids; thus:

Hydrocarbons.	Alcohols.	Acids.
C_nH_{2n+2}	$C_nH_{2n+2}O$	$C_nH_{2n}O_2$
C_nH_{2n}	$C_nH_{2n}O$	$C_nH_{2n-2}O_2$
C_nH_{2n-2}	$C_nH_{2n-2}O$	$C_nH_{2n-4}O_2$
C_nH_{2n-4}	$C_nH_{2n-4}O$	$C_nH_{2n-6}O_2$
&c.	&c.	&c.

The best known monatomic acids are those belonging to the series $C_nH_{2n}O_2$, $C_nH_{2n-2}O_2$, $C_nH_{2n-8}O_2$, and $C_nH_{2n-10}O_2$. Of the other series only a few terms have hitherto been obtained.

1. — Acids belonging to the series $C_nH_{2n}O_2$, or $C_nH_{2n-1}O(OH)$.

These acids are called *fatty* or *adipic acids*, most of them being of an oily consistence, and the higher members of the series solid fats. The following is a list of the known acids of the series, together with their melting and boiling points.

Name.	Formula.	Melting point.	Boiling point.
Formic acid	CH_2O_2	+1° C. (34° F.)	100° C. (212° F.)
Acetic acid	$C_2H_4O_2$	+17° " (62° ")	117° " (242° ")
Propionic acid	$C_3H_6O_2$	— —	141° " (286° ")
Butyric acid	$C_4H_8O_2$	below −20° C. (−4° F.)	161° " (322° ")
Valeric acid	$C_5H_{10}O_2$	— —	175° " (347° ")
Caproic acid	$C_6H_{12}O_2$	+5° C. (41° F.)	198° " (389° ")
Œnanthylic acid	$C_7H_{14}O_2$	— —	212° " (414° ")
Caprylic acid	$C_8H_{16}O_2$	+14° C. (57° F.)	236° " (457° ")
Pelargonic acid	$C_9H_{18}O_2$	+18° " ? (64° ")	260° " (500° ")
Rutic or Capric acid	$C_{10}H_{20}O_2$	+30° " (86° ")	— —
Lauric acid	$C_{12}H_{24}O_2$	+43·6° " (110° ")	
Myristic acid	$C_{14}H_{28}O_2$	53·8° " (129° ")	
Palmitic acid	$C_{16}H_{32}O_2$	62° " (144° ")	
Margaric acid	$C_{17}H_{34}O_2$	59·9° " ? (140° ")	
Stearic acid	$C_{18}H_{36}O_2$	69·2° " (157° ")	
Arachidic acid	$C_{20}H_{40}O_2$	75° " (167° ")	
Behenic acid	$C_{22}H_{44}O_2$	76° " (169° ")	
Cerotic acid	$C_{27}H_{54}O_2$	78°" (172° ")	
Melissic acid	$C_{30}H_{60}O_2$	88° " (190° ")	

These acids may be represented on the marsh-gas type and on the water-type by the following formulæ:

	Type.	*Acid.*
Marsh-gas . .	$C\begin{cases}H\\H\\H\\H\end{cases}$	$C\begin{cases}(C_{n-1}H_{2n-1}'\\O\\OH\end{cases}$ or $\begin{matrix}C_{n-1}H_{2n-1}\\\vert\\O{=}C{-}OH\end{matrix}$
Water . .	$\left.\begin{matrix}H\\H\end{matrix}\right\}O$ or HOH	$(C_nH_{2n-1}\overset{H}{O})'\Big\}O$ or $(C_nH_{2n-1}O)'OH$.

If in either of these formulæ we make n successively equal to 1, 2, 3, &c., we get the formulæ of formic, acetic, propionic, &c. acid; thus:

$C\begin{cases}H\\O''\\OH\end{cases}$	$C\begin{cases}CH_3\\O''\\OH\end{cases}$	$C\begin{cases}C_2H_5\\O''\\OH\end{cases}$	$C\begin{cases}C_3H_7\\O''\\OH\end{cases}$	$C\begin{cases}C_4H_9\\O''\\OH\end{cases}$
Formic.	Acetic.	Propionic.	Butyric.	Valeric.

The acid radicals $C_nH_{2n-1}O$, in the water-type formulæ, may be regarded as compounds of carbonyl with alcohol radicals, $C_nH_{2n-1}O = CO(C_{n-1}H_{2n-1})$, and accordingly the several acids may be represented as follows:

$\left.\begin{matrix}COH\\H\end{matrix}\right\}O$	$\left.\begin{matrix}CO(CH_3)\\H\end{matrix}\right\}O$	$\left.\begin{matrix}CO(C_2H_5)\\H\end{matrix}\right\}O$ &c.
Formic.	Acetic.	Propionic.

All the acids of the series containing more than three carbon-atoms admit of isomeric modifications, according to the constitution of the alcohol-radical which they contain: butyric acid, $C_5H_8O_2$, for example, may exhibit the following modifications:

Normal butyric acid.

$$\begin{matrix}CH_2CH_2CH_3\\\vert\\O{=}C{-}OH\end{matrix} \quad \text{or} \quad \begin{matrix}CH_3\\\vert\\CH_2\\\vert\\CH_2\\\vert\\O{=}C{-}OH\end{matrix}$$

Isobutyric acid.

$$\begin{matrix}CH(CH_3)_2\\\vert\\O{=}C{-}OH\end{matrix} \quad \text{or} \quad \begin{matrix}H_3C\ CH_3\\\diagdown\ \diagup\\CH\\\vert\\O{=}C{-}OH\end{matrix}$$

But none of these acids can exhibit modifications analogous to the secondary and tertiary alcohols: because in them the carbon-atom which is associated with hydroxyl has two of its other units of equivalence satisfied by an atom of bivalent oxygen, and therefore cannot unite directly with more than one other atom of carbon. Accordingly, it is found that the secondary and tertiary alcohols are not converted by oxidation into acids containing the same number of carbon-atoms as themselves.

Occurrence. — Most of the fatty acids are found in the bodies of plants or animals, some in the free state: formic acid in ants and nettles: valeric acid in valerian root; pelargonic acid in the essential oil of *Pelargonium roseum;* and cerotic acid in bees'-wax. Others occur as ethereal salts of monatomic or polyatomic alcohols: as cetyl palmitate in spermaceti; ceryl cerotate in Chinese wax; glyceric butyrate, palmitate, stearate, &c., in natural fats.

Formation. — 1. By oxidation of the primary alcohols of the methyl series, as by exposure to the air in contact with platinum black, or by heating with aqueous chromic acid. — 2. By the oxidation of aldehydes. In this case an atom of oxygen is simply added; *e. g.*, C_2H_4O (aldehyde) + O = $C_2H_4O_2$ (acetic acid).

3. By the action of carbon dioxide on the potassium or sodium compound of an alcohol-radical of the methyl series; thus,

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Sodium methide.}}{CH_3Na} = \underset{\text{Sodium acetate.}}{\begin{matrix}CH_3\\|\\COONa\end{matrix}}$$

4. By the action of alkalies or acids on the cyanides of the alcohol-radicals; C_nH_{2n+1}: thus,

$$\underset{\text{Alcoholic cyanide.}}{\begin{matrix}C_nH_{2n+1}\\|\\CN\end{matrix}} + \underset{\text{Potassium hydrate.}}{KOH} + \underset{\text{Water.}}{OH_2} = \underset{\text{Potassium-salt of fatty acid.}}{\begin{matrix}C_nH_{2n+1}\\|\\COOK\end{matrix}} + \underset{\text{Ammonia.}}{NH_3}$$

and:

$$\underset{\text{Alcoholic cyanide.}}{\begin{matrix}C_nH_{2n+1}\\|\\CN\end{matrix}} + \underset{\text{Hydrochloric acid.}}{HCl} + \underset{\text{Water.}}{2OH_2} = \underset{\text{Potassium salt.}}{\begin{matrix}C_nH_{2n+1}\\|\\COOH\end{matrix}} + \underset{\text{Ammonium chloride.}}{NH_4Cl}$$

In this manner the cyanide of each alcohol-radical yields the potassium salt of the acid next higher in the series, that is, containing one atom of carbon more; methyl cyanide, for example, yielding acetic acid, ethyl cyanide, yielding propionic acid, &c.; thus,

$$\underset{\text{Methyl cyanide.}}{\begin{matrix}CH_3\\|\\CN\end{matrix}} + KOH + OH_2 = \underset{\text{Potassium acetate.}}{\begin{matrix}CH_3\\|\\COOK\end{matrix}} + NH_3$$

5. By the action of water on the corresponding acid chlorides; *e. g.*,

$$\underset{\text{Acetyl chloride.}}{C_2H_3OCl} + HOH = HCl + \underset{\text{Acetic acid.}}{C_2H_3O(OH)}$$

Now, these acid chlorides can be produced, in some instances at least, by the action of carbonyl chloride (phosgene gas) on thecorresponding paraffins;* thus,

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Carbonyl chloride.}}{COCl_2} = HCl + \underset{\text{Acetyl chloride.}}{C_2H_3OCl}$$

$$\underset{\text{Quartane.}}{C_4H_{10}} + \underset{\text{Carbonyl chloride.}}{COCl_2} = HCl + \underset{\text{Valeryl chloride.}}{C_5H_9OCl}$$

By these combined reactions, therefore, the paraffins may be converted into the corresponding fatty acids.

6. By the following reaction, the fatty acids may be built up one from the other, starting from acetic acid.† Ethyl acetate, treated with sodium, gives up one atom of radical hydrogen in exchange for that metal:

$$2\underset{\text{Ethyl acetate.}}{\begin{matrix}CH_3\\|\\COOC_2H_5\end{matrix}} + Na_2 = 2\underset{\text{Monosodic ethyl acetate.}}{\begin{matrix}CH_2Na\\|\\COOC_2H_5\end{matrix}} + H_2$$

* *Harnitz-Harnitzky*, Ann. Ch. Pharm. cxxxvi. 121.
† *Frankland* and *Duppa*, Proceed. Roy. Soc. xiv. 198, 458; xv. 37.

By acting on this body with the iodide of a radical, C_nH_{2n+1}, ethylic ethers of the higher acids may be produced; thus,

$$\begin{array}{ccccccc} CH_2Na & & & & & & CH_2CH_3 \\ | & + & CH_3I & = & NaI & + & | \\ COOC_2H_5 & & & & & & COOC_2H_5 \\ \text{Monosodic} & & \text{Methyl} & & & & \text{Ethyl} \\ \text{ethyl acetate.} & & \text{iodide.} & & & & \text{propionate.} \end{array}$$

If ethyl iodide were used instead of methyl iodide, the product would be ethyl butyrate, $C_4H_7O_2C_2H_5$. It has not been found possible to produce, by this reaction, the higher acids of the series from formic acid.

The six modes of formation above given are general, or capable of being made so. There are also special methods of producing particular acids of the series, but in most of these cases the reactions cannot be distinctly traced; thus formic, acetic, propionic, butyric, and valeric acids are produced by the oxidation of albumin, fibrin, casein, gelatin, and other similar substances: propionic and butyric acids in certain kinds of fermentation; acetic acid by the destructive distillation of wood and other vegetable substances.

Properties. — Most of the fatty acids are, at ordinary temperatures, transparent and colorless liquids; formic and acetic acids are watery; propionic acid and the higher acids, up to pelargonic acid, are oily; rutic acid and those above it are solid at ordinary temperatures, most of them being crystalline fats; cerotic and melissic acids are of waxy consistence. By inspecting the table on page 597, it will be seen that the boiling points of these acids differ, for the most part, by 24° C. (43° F.) for each addition of CH_2. There are, however, a few exceptions to this rule, some of which may arise from the existence of isomeric modifications. The boiling points of formic and acetic acids, however, which cannot exhibit any such modifications, differ by only 17° C. (30° F.).

Reactions. — 1. When the fatty acids are submitted to the action of *nascent oxygen* evolved by electrolysis, the oxatyl (COOH) contained in them, is resolved into water and carbon dioxide, and the alcohol radical is set free; thus,

$$\begin{array}{ccccccccc} 2 & C_4H_9 & & & & & & C_4H_9 \\ & | & + & O & = & OH_2 & + & 2CO_2 & + & | \\ & COOH & & & & & & & & C_4H_9 \\ & \text{Valeric acid.} & & & & & & & & \text{Diquartyl.} \end{array}$$

2. When the ammonium salt of either of these acids is heated with *phosphoric oxide*, it gives up water and is converted into the cyanide of the alcohol-radical next below it, *e. g.*,

$$\begin{array}{ccccc} CH_3 & & & & CH_3 \\ | & - & 2OH_2 & = & | \\ COONH_4 & & & & CN \\ \text{Ammonium} & & & & \text{Methyl} \\ \text{acetate.} & & & & \text{cyanide.} \end{array}$$

This reaction is the converse of the fourth mode of formation above given.

3. By distilling the potassium salt of a fatty acid with an equivalent quantity of *potassium formate*, the corresponding *aldehyde* is obtained:

$$\begin{array}{ccccccc} COCH_3\}O & + & COH\}O & = & CO(CH_3)H & + & CO_3K_2; \\ K & & K & & & & \\ \text{Potassium} & & \text{Potassium} & & \text{Aldehyde.} & & \text{Potassium} \\ \text{acetate.} & & \text{formate.} & & & & \text{carbonate.} \end{array}$$

and the aldehyde, treated with nascent hydrogen, is converted into a primary alcohol:

$$\underset{\text{Aldehyde.}}{CH_3\cdot COH} + H_2 = \underset{\text{Alcohol.}}{CH_3\cdot CH_2OH}$$

4. By subjecting the barium or calcium salt of a fatty acid to dry distillation, a similar decomposition takes place, resulting in the formation of a *ketone:*

$$\underset{\text{Calcium acetate.}}{(COCH_3)_2Ca''}O_2 = \underset{\text{Acetone.}}{CO(CH_3)_2} + \underset{\text{Calcium carbonate.}}{CO_3Ca''};$$

and the ketone, treated with nascent hydrogen, yields a secondary alcohol:

$$\underset{\text{Acetone.}}{CH_3\cdot COCH_3} + H_2 = \underset{\text{Secondary propyl alcohol.}}{H_3C\ CH_3\ \vee\ CHOH}$$

By these reactions, the fatty acids may be converted into alcohols.

5. The fatty acids, heated with *alcohols* in sealed tubes, yield compound ethers, or *ethereal salts*, water being eliminated:

$$\underset{\text{Butyric acid.}}{C_4H_7O(OH)} + \underset{\text{Ethyl alcohol.}}{HOC_2H_5} = OH_2 + \underset{\text{Ethyl butyrate.}}{C_4H_7O(OC_2H_5)}$$

The conversion, however, is never complete, a portion, both of the acid and of the alcohol, remaining unaltered in whatever proportion they may be mixed.

The ethereal salts of the fatty acids are, for the most part, more easily obtained by acting upon the alcohol with an acid chloride, or by passing hydrochloric acid gas into a solution of the fatty acid in the alcohol:

$$\underset{\text{Butyric chloride.}}{C_4H_7OCl} + \underset{\text{Ethyl alcohol.}}{HOC_2H_5} = HCl + \underset{\text{Ethyl butyrate.}}{C_4H_7O(OC_2H_5)}$$

Another method very commonly adopted is, to distil a potassium salt of the fatty acid with a mixture of the alcohol and strong sulphuric acid. In this case an acid sulphuric ether is first formed (as ethyl-sulphuric acid from ethyl alcohol, p. 527), and this acts upon the salt of the fatty acid in the manner illustrated by the equation:

$$\underset{\text{Ethyl-sulphuric acid.}}{SO_2(OH)(OC_2H_5)} + \underset{\text{Potassium butyrate.}}{C_4H_7O(OK)} = \underset{\text{Ethyl butyrate.}}{C_4H_7O(OC_2H_5)} + \underset{\text{Acid potassium sulphate.}}{SO_2(OH)(OK)}$$

The ethereal salts of the fatty acids are either volatile, oily, or syrupy liquids, or crystalline solids, for the most part insoluble in water, but soluble in alcohol and in ether. When distilled with potash or soda, they take up water and are saponified, that is to say resolved into the alcohol and acid; *e. g.*,

$$\underset{\text{Ethyl butyrate.}}{C_4H_7O(OC_2H_5)} + \underset{\text{Water.}}{HOH} = \underset{\text{Butyric acid.}}{C_4H_7O(OH)} + \underset{\text{Ethyl alcohol.}}{C_2H_5(OH)}$$

6. The fatty acids are strongly acted upon by the *chlorides, bromides, oxychlorides,* and *oxybromides of phosphorus,* yielding *acid chlorides* and *bromides,* the phosphorus being at the same time converted into phosphorous or phosphoric acid; thus,

$$\underset{\text{Acetic acid.}}{3C_2H_3O(OH)} + \underset{\substack{\text{Phosphorus}\\\text{trichloride.}}}{PCl_3} = \underset{\substack{\text{Phosphorus}\\\text{acid.}}}{PO_3H_3} + \underset{\substack{\text{Acetic}\\\text{chloride.}}}{3C_2H_3OCl}$$

$$\underset{\text{Acetic acid.}}{3C_2H_3O(OH)} + \underset{\substack{\text{Phosphorus}\\\text{oxybromide.}}}{PCl_3O} = \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{PO_4H_3} + \underset{\substack{\text{Acetic}\\\text{chloride.}}}{3C_2H_3OCl}$$

$$\underset{\text{Acetic acid.}}{C_2H_3O(OH)} + \underset{\substack{\text{Phosphorus}\\\text{pentachloride.}}}{PCl_5} = \underset{\substack{\text{Phosphoric}\\\text{oxychloride.}}}{PCl_3O} + \underset{\substack{\text{Hydro-}\\\text{chloric acid.}}}{HCl} + \underset{\substack{\text{Acetic}\\\text{chloride.}}}{C_2H_5OCl}$$

These acid chlorides are, for the most part, oily liquids, having a pungent acid odor; they are easily decomposed by water, yielding the fatty acid and hydrochloric acid. This decomposition takes place also when they are exposed to the air: hence they emit dense acid fumes. They react in an exactly similar manner with alcohols, as above mentioned, yielding hydrochloric acid and a compound ether.

7. The chlorides of the acid radicals, $C_n H_{2n-1}O$, act violently on ammonia, forming ammonium chloride, and the *amide* corresponding to the acid from which they are derived; *e. g.*,

$$\underset{\substack{\text{Acetic}\\\text{chloride.}}}{C_2H_3OCl} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\substack{\text{Ammonium}\\\text{chloride.}}}{NH_4Cl} + \underset{\text{Acetamide.}}{NH_2(C_2H_3O)}$$

8. The acid chlorides, distilled with a metallic salt of the corresponding acid, yield a metallic chloride and the *oxide* or *anhydride* corresponding to the acid: thus,

$$\underset{\substack{\text{Acetic}\\\text{chloride.}}}{C_2H_3OCl} + \underset{\substack{\text{Potassium}\\\text{acetate.}}}{C_2H_3O(OK)} = KCl + \underset{\substack{\text{Acetic}\\\text{oxide.}}}{(C_2H_3O)_2O}$$

In like manner, when distilled with the potassium salt of another monatomic acid, they yield oxides or anhydrides containing two monatomic acid radicals; *e. g.*,

$$\underset{\substack{\text{Acetic}\\\text{chloride.}}}{C_2H_3OCl} + \underset{\substack{\text{Potassium}\\\text{benzoate.}}}{C_7H_5O(OK)} = KCl + \underset{\substack{\text{Aceto-ben-}\\\text{zoic oxide.}}}{\left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O}$$

The oxides of the fatty acid radicals may also be prepared by heating a dry lead-salt of the acid, in a sealed tube, with carbon bisulphide; *e. g.*,

$$\underset{\text{Lead acetate.}}{2\,Pb\left\{\begin{matrix}OC_2H_3O\\OC_2H_3O\end{matrix}\right.} + CS_2 = 2PbS + CO_2 + \underset{\substack{\text{Acetic}\\\text{oxide.}}}{2(C_2H_3O)_2O}$$

The oxides of the fatty acid radicals are gradually decomposed by water, quickly when heated, yielding two molecules of the corresponding acid:

$$(C_2H_3O)_2O + OH_2 = 2C_2H_3O(OH)$$

Those containing two acid radicals yield one molecule of each of the corresponding acids.

In contact with *alcoholic oxides* (*oxygen ethers*), the acid oxides are converted into ethereal salts:

$$\underset{\text{Acetic oxide.}}{(C_2H_3O)_2O} + \underset{\text{Ethyl oxide.}}{(C_2H_5)_2O} = \underset{\text{Ethyl acetate.}}{2C_2H_3O(OC_2H_5)}$$

With *alcohols*, in like manner, they yield a mixture of a compound ether with the acid:

$$\underset{\text{Acetic oxide.}}{(C_2H_3O)_2O} + \underset{\text{Ethyl alcohol.}}{C_2H_5(OH)} = \underset{\text{Ethyl acetate.}}{C_2H_3O(OC_2H_5)} + \underset{\text{Acetic acid.}}{C_2H_3O(OH)}$$

The acid oxides are decomposed by *ammonia gas*, yielding a mixture of an ammonium-salt with an *amide:*

$$\underset{\text{Acetic oxide.}}{(C_2H_3O)_2O} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Ammonium acetate.}}{C_2H_3O(ONH_4)} + \underset{\text{Acetamide.}}{NH_2C_2H_3O}$$

9. The fatty acids, subjected to the action of *chlorine* or *bromine*, give off hydrochloric or hydrobromic acid, and are converted into substitution-compounds containing one or more atoms of chlorine or bromine in place of hydrogen; but it is only the hydrogen within the radical that can be thus exchanged, the typic hydrogen remaining unaltered, so that the number of chlorine or bromine-atoms introduced in place of hydrogen is always less by at least one than the number of hydrogen-atoms in the acid:

$$\underset{\text{Acetic acid.}}{C_2H_3O(OH)} + Cl_2 = HCl + \underset{\text{Chloracetic acid.}}{C_2H_2ClO(OH)}$$

$$\underset{\text{Acetic acid.}}{C_2H_3O(OH)} + 3Cl_2 = 3HCl + \underset{\text{Trichloracetic acid.}}{C_2Cl_3O(OH)}$$

The *iodated acids* of the same series (or rather their ethereal salts) are obtained by heating the corresponding bromine-compounds with potassium iodide:

$$\underset{\text{Ethyl-brom-acetate.}}{C_2H_2BrO(OC_2H_5)} + KI = KBr + \underset{\text{Ethyl-iodacetate.}}{C_2H_2IO(OC_2H_5)};$$

and the ethers treated with potash yield potassium salts of the iodated acids, from which the acids may be obtained by decomposition with sulphuric acid.

The chlorinated and brominated fatty acids, boiled with *water* and *silver oxide*, exchange the whole of their chlorine or bromine for an equivalent quantity of hydroxyl, producing new acids, which differ from the primitive acids by a number of atoms of oxygen equal to the number of atoms of chlorine or bromine present; *e. g.*,

$$\underset{\text{Bromacetic acid.}}{2C_2H_3BrO_2} + Ag_2O + H_2O = 2AgBr + \underset{\text{Glycollic acid.}}{2C_2H_4O_3}$$

$$\underset{\text{Dibromo-butyric acid.}}{C_4H_6Br_2O_2} + Ag_2O + H_2O + 2AgBr + \underset{\text{Dioxy-butyric acid.}}{C_4H_8O_4},$$

Dichloracetic and trichloracetic acid are not sufficiently stable to exhibit this transformation, their molecules splitting up altogether when boiled with silver oxide.

The monochlorinated and monobrominated acids, subjected to the action of an alcoholic solution of *ammonia gas*, yield ammonium chloride and a new

acid, in which the chlorine or bromine is replaced by amidogen. Thus monochloracetic acid yields *amidacetic acid*, or *glycocine*:

$$\underset{\text{Chloracetic acid.}}{C_2H_3ClO_2} + 2NH_3 = NH_4Cl + \underset{\text{Amidacetic acid.}}{C_2H_3(NH_2)O_2}$$

There is another way of viewing these amidated acids which will be considered hereafter.

Formic Acid, $CH_2O_2 = CHO(OH) = C\begin{cases} H \\ O'' = \\ OH \end{cases}\begin{matrix} H \\ | \\ COOH \end{matrix}$.—This acid occurs in the concentrated state in the bodies of ants, in the hairs and other parts of certain caterpillars, and in stinging nettles. It may be produced by the first, second, and fourth of the above-mentioned general methods of forming the fatty acids—viz., by the slow oxidation of methyl alcohol, or of formic aldehyde, in contact with platinum black, and as a potassium salt by heating hydrocyanic acid (hydrogen cyanide) with an alcoholic solution of potash:

$$\underset{\text{Hydrogen cyanide.}}{HCN} + KOH + OH_2 = NH_3 + \underset{\text{Potassium formate.}}{CHO(OK)}$$

It is also produced by certain special reactions—viz: *α*. By passing carbon monoxide over moist potassium hydrate, the gas being thereby absorbed, and producing potassium formate:

$$CO + HOK = COH(OK)$$

The absorption of the gas is accelerated by the presence of a considerable quantity of water, and still more by alcohol or ether.

β. By distilling dry oxalic acid mixed with sand or pumice-stone, or better with glycerin:

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} = \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Formic acid.}}{CH_2O_2}$$

The distillation of oxalic acid with glycerine is a very advantageous mode of preparing formic acid. The glycerine takes no part in the decomposition, but appears to act by preventing the temperature from rising too high: when oxalic acid is distilled alone or with sand, the greater part of the formic acid produced is resolved into water and carbon monoxide.

γ. By passing carbon dioxide and water-vapor over potassium at a moderate heat, acid potassium carbonate being formed at the same time:

$$K_2 + 2CO_2 + OH_2 = \underset{\text{Acid carbonate.}}{CO_3KH} + \underset{\text{Formate.}}{CHO_2K}$$

δ. By the oxidation of sugar, starch, gum, and organic substances in general. A convenient mode of preparation is the following: 1 part of sugar, 3 parts of manganese dioxide, and 2 parts of water, are mixed in a very capacious retort, or large metal still; 3 parts of oil of vitriol, diluted with an equal weight of water, are then added, and when the first violent effervescence from the disengagement of carbon dioxide has subsided, heat is cautiously applied, and a considerable quantity of liquid distilled over. This is very impure: it contains a volatile oily matter, and some substance which communicates a pungency not proper to formic acid in that dilute state. The acid liquid is neutralized with sodium carbonate, and the re-

sulting formate purified by crystallization, and, if needful, by animal charcoal. From this, or any other of its salts, solution of formic acid may be readily obtained by distillation with dilute sulphuric acid.

To obtain the acid in its most concentrated state, the dilute acid is saturated with lead oxide, the liquid is evaporated to complete dryness, and the dried lead formate, reduced to fine powder, is very gently heated in a glass tube connected with a condensing apparatus, through which a current of dry sulphuretted hydrogen gas is transmitted. It forms a clear, colorless liquid, which fumes slightly in the air, has an exceedingly penetrating odor, boils at 98·3° C. (210° F.), and crystallizes in large brilliant plates when cooled below 0°. The specific gravity of the acid is 1·235; it mixes with water in all proportions: the vapor is inflammable, and burns with a blue flame. Concentrated formic acid is extremely corrosive, attacking the skin, and forming a blister or an ulcer, painful and difficult to heal.

Formic acid mixes with water in all proportions. The aqueous acid has an odor and taste much resembling those of acetic acid: it reddens litmus strongly, and decomposes alkaline carbonates with effervescence. Formic acid likewise dissolves readily in alcohol, being partly converted into ethyl formate.

Formic acid is a powerful reducing agent. It may be readily distinguished from acetic acid by heating it with solution of *silver nitrate;* the metal is thus reduced, sometimes in the pulverulent state, sometimes as a specular coating on the glass tube, and carbon dioxide is evolved. Mercuric chloride is reduced by formic acid to calomel. Formic acid heated with *oil of vitriol* splits up into water and carbon monoxide, $CH_2O_2 = OH_2 + CO$.

Chlorine converts it into hydrochloric acid and carbon dioxide:

$$CH_2O_2 + Cl_2 = 2HCl + CO_2$$

Formic acid heated with strong *bases* is converted into oxalic acid, with disengagement of hydrogen:

$$\underset{\text{Formic acid.}}{2CH_2O_2} + \underset{\text{Baryta.}}{BaO} = \underset{\text{Barium oxalate.}}{C_2BaO_4} + H_2 + OH_2.$$

Formates. — The composition of these salts is expressed by the formulæ, CHO_2M, $(CHO_2)_2M''$, $(CHO_2)_3M'''$, &c., according to the equivalent value of the metal or other positive radical contained in them. They are all soluble in water: their solutions form dark-red mixtures with ferric salts. When distilled with strong sulphuric acid they give off acid carbon monoxide, and leave a residue of sulphate. The formates of the alkali-metals heated with the corresponding salts of other fatty acids, yield a carbonate and an aldehyde (p. 600).

Sodium formate crystallizes in rhombic prisms containing CHO_2Na. Aq. It reduces many metallic oxides when fused with them. *Potassium formate,* CHO_2K, is difficult to crystallize, on account of its great solubility. *Ammonium formate* crystallizes in square prisms: it is very soluble, and is decomposed at high temperatures into hydrocyanic acid and water, the elements of which it contains: $CHO_2NH_4 = 2OH_2 + CNH$. The formates of *barium, strontium, calcium,* and *magnesium* form small prismatic, easily soluble crystals. *Lead formate* crystallizes in small, diverging, colorless needles, which require for solution 40 parts of cold water. The *manganous, ferrous, zinc, nickel,* and *cobalt formates* are also crystallizable. *Cupric formate* is very beautiful, constituting bright-blue rhombic prisms of considerable magnitude. *Silver formate* is white, but slightly soluble, and decomposed by the least elevation of temperature.

Methyl formate, CHO_2CH_3, isomeric with acetic acid, is prepared by heating in a retort equal weights of neutral methyl sulphate and sodium formate. It is a very volatile liquid, lighter than water, boiling between 36° and 38°.

Ethyl formate, $CHO_2C_2H_5$, isomeric with methyl acetate and propionic acid (p. 475), is prepared by distilling a mixture of 7 parts of dry sodium formate, 10 of oil of vitriol, and 6 of strong alcohol. The formic ether, separated by the addition of water to the distilled product, is agitated with a little magnesia, and left for several days in contact with calcium chloride. Ethyl formate is colorless, has an aromatic odor, a density of 0·915, and boils at 56° C. (133° F.). Water dissolves it to a small extent.

Acetic Acid, $C_2H_4O_2 = C_2H_3O(OH)$, or $COCH_3(OH) = C\left\{\begin{matrix} CH_3 \\ O'' \\ OH \end{matrix}\right. = \begin{matrix} CH_3 \\ | \\ COOH \end{matrix}$.—

This acid is found in small quantities in the juices of plants and in animal fluids. It may be produced by either of the first five general methods of formation given on pages 598, 599, and in particular by the slow oxidation of alcohol. When spirit of wine is dropped upon platinum black, the oxygen condensed in the pores of the latter reacts so powerfully upon the alcohol as to cause its instant inflammation. When the spirit is mixed with a little water, and slowly dropped upon the finely divided metal, oxidation still takes place, but with less energy, and vapor of acetic acid is abundantly evolved. In all these modes of formation, the acetic acid is ultimately producible from inorganic materials. It is also formed by the action of nascent hydrogen on trichloracetic acid, which may itself be produced from inorganic materials. Lastly, acetic acid is obtained, together with many other products, in the destructive distillation of wood and other vegetable substances.

Preparation.—1. Dilute alcohol, mixed with a little yeast, or almost any azotized organic matter susceptible of putrefaction, and exposed to the air, speedily becomes oxidized to acetic acid. Acetic acid is thus manufactured in Germany, by suffering such a mixture to flow over wood-shavings steeped in a little vinegar, contained in a large cylindrical vessel through which a current of air is made to pass. The greatly extended surface of the liquid expedites the change, which is completed in a few hours. No carbonic acid is produced in this reaction.

The best vinegar is made from wine by spontaneous acidification in a partially filled cask to which the air has access. Vinegar is first introduced into the empty vessel, and a quantity of wine added; after some days, a second portion of wine is poured in, and after similar intervals, a third and a fourth. When the whole has become vinegar, a quantity is drawn off equal to that of the wine employed, and the process is recommenced. The temperature of the building is kept up to 30° C. (86° F.). Such is the plan adopted at Orleans.* In England, vinegar is prepared from a kind of beer made for the purpose. The liquor is exposed to the air in half empty casks, loosely stopped, until acidification is complete. Frequently a little sulphuric acid is afterwards added, with the view of checking further decomposition, or *mothering*, by which the product would be spoiled.

When dry, hard wood, as oak and beech, is subjected to destructive distillation at a red heat, acetic acid is found among the liquid condensable products of the operation. The distillation is conducted in an iron cylinder of large dimensions, to which a worm or condenser is attached; a sour watery liquid, a quantity of tar, and much inflammable gas pass over, while charcoal of excellent quality remains in the retort. The acid liquid is subjected to distillation, the first portion being collected apart for the

* *Dumas*, Chimie appliqué aux Arts, vi. 537.

preparation of wood-spirit. The remainder is saturated with lime, concentrated by evaporation, and mixed with the solution of sodium sulphate; calcium sulphate is thereby precipitated, while the acetic acid is transferred to the soda. The filtered solution is evaporated to its crystallizing point; and the crystals are drained as much as possible from the dark, tarry mother-liquor, and deprived by heat of their combined water. The dry salt is then cautiously fused, by which the last portions of tar are decomposed or expelled: it is then re-dissolved in water, and re-crystallized. Pure sodium acetate, thus obtained, readily yields acetic acid by distillation with sulphuric acid.

The strongest acetic acid is prepared by distilling finely powdered anhydrous sodium acetate with three times its weight of concentrated oil of vitriol. The liquid is purified by rectification from sodium sulphate accidentally thrown up, and exposed to a low temperature. Crystals of pure acetic acid, $C_2H_4O_2$, then form in large quantity: they may be drained from the weaker fluid portion, and suffered to melt. Below 15·5° C. (60° F.) this substance, often called *glacial acetic acid*, forms large, colorless, transparent crystals, which above that temperature fuse to a thin, colorless liquid, of exceedingly pungent and well-known odor: it raises blisters on the skin. It is miscible in all proportions with water, alcohol, and ether, and dissolves camphor and several resins. When diluted it has a pleasant acid taste. Glacial acetic acid in the liquid state has a density of 1·063, and boils at 120° C. (248° F.). Its vapor is inflammable, and exhibits the variations of density noticed at page 461. At 300° C. (572° F.), or above, it is 2·08 compared with air, or 30° compared with hydrogen, agreeing exactly with the theoretical density, which is half the molecular weight; but at temperatures near the boiling point it is considerably greater, being 2·90 at 140° C. (284° F.), and 3·20 at 125° C. (257° F.) (referred to air).

Dilute acetic acid, or distilled vinegar, used in pharmacy, should always be carefully examined for copper and lead; these impurities are contracted from the metallic vessel or condenser sometimes employed in the process. The strength of any sample of acetic acid cannot be safely inferred from its density, but it is easily determined by observing the quantity of dry sodium carbonate necessary to saturate a known weight of the liquid.

Acetic acid exhibits all the reactions of the fatty acids in general (pp. 601–604). The acid itself does not readily conduct the electric current, but a solution of potassium acetate is decomposed by electrolysis, with formation of dimethyl or ethane:

$$2\left|\begin{matrix}CH_3\\COOK\end{matrix}\right. + OH_2 = C_2H_6 + H_2 + CO_2 + CO(OK)_2$$

Potassium acetate. — Ethane. — Potassium carbonate.

Acetic acid is not attacked by nitric acid, but *periodic acid* converts it by oxidation into formic acid and carbon dioxide, being itself reduced to iodic acid or even to free iodine:

$$C_2H_4O_2 + O_3 = CH_2O_2 + CO_2 + OH_2.$$

Potassium acetate distilled with *arsenious oxide* gives off a highly inflammable and characteristically fetid oil, consisting chiefly of arsendimethyl or cacodyl, $As_2(CH_3)_4$.

Acetates.—Acetic acid forms a large number of highly important salts, represented by the formulæ, $C_2H_3O_2M$, $(C_2H_3O_2)_2M''$, or $(C_2H_3O_2)_3M'''$, according to the equivalent value of the metals contained in them. Being a monobasic acid, it cannot form any acid salts properly so called, that is by

replacement of a *part* of its typic hydrogen (p. 282); but the normal acetates of the alkali-metals can take up a molecule of acetic acid, just as they take up water of crystallization, forming salts called *acid acetates* or *diacetates*, $C_2H_3O_2M \cdot C_2H_4O_2$. There are also basic acetates formed by the union of a molecule of a normal acetate with a molecule of metallic oxide or hydrate.

Potassium Acetates.—The *normal salt*, $C_2H_3O_2K$, crystallizes with great difficulty: it is generally met with as a foliated, white, crystalline mass, obtained by neutralizing potassium carbonate with acetic acid, evaporating to dryness, and heating the salt to fusion. It is extremely deliquescent, and soluble in water and alcohol: the solution is usually alkaline from a little loss of acid by the heat to which it has been subjected. From the alcoholic solution, potassium carbonate is thrown down by a stream of carbon dioxide.

The *acid salt*, $C_2H_3O_2K \cdot C_2H_4O_2$, is formed by evaporating a solution of the neutral salt in excess of acetic acid, and crystallizes by slow evaporation in long flattened prisms. It is very deliquescent, and decomposes at 200°, giving off crystallizable acetic acid.

Sodium Acetate, $C_2H_3O_2Na \cdot 3$ Aq.—The mode of preparation of this salt on the large scale has been already described: it forms large, transparent, colorless crystals, derived from a rhombic prism, which are easily rendered anhydrous by heat, effloresce in dry air, and dissolve in 3 parts of cold, and in an equal weight of hot water: it is also soluble in alcohol. The taste of this salt is cooling and saline. The dry salt melts at 288° C. (550° F.), and begins to decompose at 315° C. (600° F.).

Ammonium Acetates.—The *neutral acetate*, $C_2H_3O_2NH_4$, is a white odorless salt obtained by saturating glacial acetic acid with dry ammonia gas. It is very difficult to obtain in the crystalline form, for its aqueous solution, when evaporated, gives off ammonia and leaves the acid salt. When distilled with phosphoric oxide, it loses 2 molecules of water, and gives off ethenyl nitrile or acetonitrile, $(C_2H_3)'''N = C_2H_3O_2NH_4 - 2OH_2$. The aqueous solution, known in the Pharmacopœia as *Spiritus Mindereri*, is prepared by saturating aqueous acetic acid with ammonia or ammonium carbonate.

The *acid salt*, $C_2H_3O_2NH_4 \cdot C_2H_4O_2$, is obtained as a crystalline sublimate by heating powdered sal-ammoniac with potassium or calcium acetate, ammonia being given off at the same time; also as a radiated crystalline mass by evaporating the aqueous solution of the neutral salt.

The acetates of *barium*, *strontium*, and *calcium* are very soluble, and can be procured in crystals; *magnesium acetate* crystallizes with difficulty.

Aluminium Acetates.—This salt is very soluble in water, and dries up in the vacuum of the air-pump to a gummy mass without trace of crystallization. If foreign salts are present, the solution of the acetate becomes turbid on heating, from the separation of a basic compound, which redissolves as the liquid cools. Aluminum acetate is much employed in calico printing: it is prepared by mixing solutions of lead acetate and alum, and filtering from the insoluble lead sulphate. The liquid is thickened with gum or other suitable material, and with it the design is impressed upon the cloth by a wood-block, or by other means. Exposure to a moderate degree of heat drives off the acetic acid, and leaves the alumina in a state capable of entering into combination with the dye-stuff.

Some very interesting researches on aluminum acetate have been published by the late Mr. Walter Crum.* The solution obtained by decompos-

* Chem. Soc. Quar. Jour. vi. 216.

ing aluminum sulphate, $(SO_4)_3Al_2$, with lead acetate, may be supposed to contain neutral aluminium acetate, $(C_2H_3O_2)_3Al'''$. This salt cannot, however, be obtained in the dry state. If the solution be rapidly evaporated at low temperatures, by being spread in thin layers on glass or porcelain, a basic *soluble* acetate is obtained, having the composition $4(C_2H_3O_2)_3Al'''.Al_2O_3.6$ aq.; but if the solution be left to stand, or submitted to the action of heat, *insoluble* basic salts are precipitated, differing in composition from the former only by containing 3 or $3\frac{1}{3}$ molecules of water instead of four.

The soluble aluminum acetate, when exposed in a dilute solution to the temperature of boiling water for several days, undergoes a very remarkable change, the whole, or nearly the whole, of the acetic acid being expelled by the action of heat, and a peculiar soluble modification of alumina (already described under ALUMINIUM, p. 335), remaining in solution.

Manganese acetate forms colorless, rhombic, prismatic crystals, permanent in the air. *Ferrous acetate* crystallizes in small, greenish-white needles, very prone to oxidation; both salts dissolve freely in water. *Ferric acetate* is a dark brownish-red, uncrystallizable liquid, of powerful astringent taste. *Cobalt acetate* forms a violet-colored, crystalline, deliquescent mass. The *nickel salt* separates in green crystals, which dissolve in 6 parts of water.

LEAD ACETATES.—The *normal salt*, $(C_2H_3O_2)_2Pb''.3$ aq., is prepared on a large scale by dissolving litharge in acetic acid: it may be obtained in colorless, transparent, prismatic crystals, but is generally met with in commerce as a confusedly crystalline mass, somewhat resembling loaf-sugar. From this circumstance and from its sweet taste, it is often called *sugar of lead*. The crystals are soluble in about $1\frac{1}{4}$ parts of cold water, effloresce in dry air, and melt when gently heated in their water of crystallization; the latter is easily driven off, and the anhydrous salt obtained, which melts, and afterward decomposes, at a high temperature. Acetate of lead is soluble in alcohol. The aqueous solution has an intensely sweet, and at the same time astringent taste, and is not precipitated by ammonia. It is an article of great value to the chemist.

Basic Acetates (Subacetates) of Lead.—A *sesquibasic acetate*, $2(C_2H_3O_2)_2Pb''.Pb''O$, is produced when the neutral anhydrous salt is so far decomposed by heat as to become converted into a porous white mass, decomposable only at a much higher temperature. It is soluble in water, and separates from the solution evaporated to a syrupy consistence in the form of crystalline scales. A *triplumbic acetate*, $(C_2H_3O_2)_2Pb''.2Pb''O$, is obtained by digesting at a moderate heat, 7 parts of finely powdered litharge, 6 parts of lead acetate, and 30 parts of water; or, by mixing a cold saturated solution of neutral lead acetate with a fifth of its volume of caustic ammonia, and leaving the whole some time in a covered vessel. The salt separates in minute needles containing one molecule of water. The solution of basic acetate prepared by the first method is known in pharmacy under the name of *Goulard water*. There is also a sexplumbic acetate, $(C_2H_3O_2)_2Pb''.5Pb''O$, formed by adding a great excess of ammonia to a solution of normal lead acetate, or by digesting the normal salt with a large quantity of oxide. It is a white, slightly crystalline substance, insoluble in cold, and but little soluble in boiling water. The solutions of the basic lead acetates have a strong alkaline reaction, and absorb carbonic acid with the greatest avidity, becoming turbid from precipitation of basic carbonate.

CUPRIC ACETATES.—The *normal acetate*, $(C_2H_3O_2)_2Cu.$ aq., is prepared by dissolving *verdigris* in hot acetic acid, and leaving the filtered solution to cool. It forms beautiful dark-green crystals, which dissolve in 14 parts of cold and 5 parts of boiling water, and are also soluble in alcohol. A solu-

tion of this salt, mixed with sugar and heated, yields cupric oxide in the form of minute red octohedral crystals: the residual copper solution is not precipitated by an alkali. Cupric acetate yields, by destructive distillation, strong acetic acid containing acetone and contaminated with copper. The salt is sometimes called *distilled verdigris*, and is used as a pigment.

Basic Cupric Acetates.—Common verdigris, made by spreading the marc of grapes upon plates of copper exposed to the air for several weeks, or by substituting, with the same view, pieces of cloth dipped in crude acetic acid, is a mixture of several basic cupric acetates which have a green or blue color. One of these, $2(C_2H_3O_2)_2Cu''.CuO.6$ aq., is obtained by digesting the powdered verdigris in warm water, and leaving the soluble part to spontaneous evaporation. It forms a blue, crystalline mass, but little soluble in cold water. When boiled, it deposits a brown powder, which is a subsalt with large excess of base. The green insoluble residue of the verdigris contains $(C_2H_3O_2)_2Cu.2CuO.3$ aq.; it may be formed by digesting normal cupric acetate with the hydrated oxide. By ebullition with water it is resolved into normal acetate and the brown basic salt.

Silver Acetate, $C_2H_3O_2Ag$, is obtained by mixing potassium acetate with silver nitrate, and washing the precipitate with cold water to remove the potassium nitrate. It crystallizes from a warm solution in small colorless needles, which have but little solubility in the cold.

Mercurous acetate forms small scaly crystals, which are as feebly soluble as those of acetate of silver. *Mercuric acetate* dissolves with facility.

Methyl Acetate, $C_2H_3O_2CH_3$, occurs in crude wood-spirit. It is prepared by distilling 2 parts of methyl alcohol with 1 part of glacial acetic acid and 1 part of sulphuric acid, or 1 part of methyl alcohol with 1 part of potassium acetate and 2 parts of sulphuric acid. When purified by rectification over calcium chloride and quick-lime, it forms a colorless fragrant liquid of sp. gr. 0·9562 at 0°, boiling at 55° or 56° C. (131°–133° F.). It dissolves in water, and mixes in all proportions with alcohol and ether.

Ethyl Acetate, $C_2H_3O_2C_2H_5$, may be prepared by heating together in a retort 3 parts of potassium acetate, 3 parts of strong alcohol, and 2 parts of oil of vitriol. The distilled product is mixed with water, to separate the alcohol, digested first with a little chalk, and afterwards with fused calcium chloride, and, lastly, rectified. The pure ether is an exceedingly fragrant limpid liquid: it has a density of 0·890, and boils at 73·8° C. (165° F.). Alkalies decompose it in the manner already mentioned (p. 601). When treated with ammonia, it yields *acetamide*, $NH_2C_2H_3O$.

Amyl Acetate, $C_2H_3O_2C_5H_{11}$, prepared in a similar manner, boils at 133° C. (272° F.). It possesses in a remarkable manner the odor of the Jargonelle pear, and is now manufactured on a large scale for flavoring liquors and confectionery.

Ethene Acetates. — These compounds may be derived from ethene alcohol (glycol) by substitution of one or two equivalents of acetyl for hydrogen. The *monacetate*, $(C_2H_4)''\left\{\begin{matrix}OH\\OC_2H_3O\end{matrix}\right.$, is produced by heating ethene dibromide with an alcoholic solution of potassium acetate. The product is distilled, the portion coming over at 182° C. (360° F.) being kept separate. It is a colorless, oily liquid, miscible in every proportion with water or alcohol. Hydrochloric acid gas passed into ethene monacetate converts it into ethene acetochloride, or glycolic chloracetin, $C_2H_4\left\{\begin{matrix}Cl\\OC_2H_3O\end{matrix}\right.$, which is precipitated, on addition of water, as an oily liquid boiling at 145° C. (293° F.). Treat-

ment with potash decomposes it into ethene oxide, potassium acetate, and potassium chloride.

Ethene diacetate, $C_2H_4\left\{\begin{matrix}OC_2H_3O\\OC_2H_3O\end{matrix}\right.$, is prepared by digesting a mixture of ethene dibromide, silver acetate, and glacial acetic acid in the water-bath, and exhausting the digested mass with ether. On distilling the ethereal solution, the ether first passes over, then the acetic acid, and lastly, when the temperature has reached 187° C. (368° F.), ethene diacetate. It is a colorless, neutral liquid, of sp. gr. 1·128, at 0°; soluble in 7 parts of water and in every proportion in alcohol and ether.

Propenyl or Glyceryl Acetates; or Acetins. — These ethers are derived from propenyl alcohol (glycerin) by substitution of 1, 2, or 3 equivalents of acetyl for hydrogen. The formula of glycerin being $(C_3H_5)'''OH_3$, those of the three acetins are:

Monoacetin . . .	$(C_3H_5)'''(OH)_2(OC_2H_3O)$
Diacetin . . .	$(C_3H_5)'''(OH)(OC_2H_3O)_2$
Triacetin . . .	$(C_3H_5)'''(OC_2H_3O)_3$

They are oily liquids, produced by heating glycerin and acetic acid together, in various proportions, in sealed tubes.

Acetic Chloride or Acetyl Chloride, C_2H_3OCl.—This compound, which has the constitution of acetic acid with chlorine substituted for hydroxyl, is produced, as already observed (p. 602), by the action of phosphorus trichloride, pentachloride, or oxychloride on glacial acetic acid. The product heated with water and dilute soda-solution, to remove phosphorus oxychloride and hydrochloric acid, and then rectified, yields acetic chloride as a colorless liquid, having a suffocating odor and emitting dense fumes of hydrochloric acid in contact with the air. It is heavier than water, boils at 55° C. (131° F.), and is decomposed by water and alkaline solutions, yielding hydrochloric and acetic acids.

Acetic Oxide or Anhydride, $C_4H_6O_3 = (C_2H_3O)_2O$, sometimes called *Anhydrous acetic acid.* — This compound is obtained:

1. By the action of acetyl chloride on potassium or sodium acetate:

$$C_2H_3O(ONa) + C_2H_3OCl = NaCl + (C_2H_3O)_2O.$$

2. By heating sodium acetate with benzoyl chloride, C_7H_5OCl, whereby benzo-acetic oxide is formed in the first instance, and subsequently resolved into acetic and benzoic oxides, the former distilling over, while the latter remains:

$$\underset{\text{Sodium acetate.}}{C_2H_3O(ONa)} + \underset{\text{Benzoyl chloride.}}{C_7H_5OCl} = NaCl + \underset{\text{Benzo-acetic oxide.}}{\left.\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O}$$

and:

$$2\underset{\text{Benzo-acetic oxide.}}{\left\{\begin{matrix}C_2H_3O\\C_7H_5O\end{matrix}\right\}O} = \underset{\text{Acetic oxide.}}{(C_2H_3O)_2O} + \underset{\text{Benzoic oxide.}}{(C_7H_5O)_2O}$$

Acetic oxide is a heavy oil which dissolves slowly in water, being gradually converted into acetic acid:

$$(C_2H_3O)_2O + OH_2 = 2C_2H_3O(OH).$$

Acids derived from Acetic Acid by Substitution.

Chloracetic Acids.— The three acids, $C_2H_3ClO_2$, $C_2H_2Cl_2O_2$, and $C_2HCl_3O_2$, are produced by the action of chlorine on acetic acid in sunshine; the second, however, is formed in small quantity only, the first or the third being produced in greatest abundance according as the acetic acid or the chlorine is in excess.

Monochloracetic acid, $C_2H_2ClO(OH)$, is produced, according to R. Hoffmann, by the action of chlorine on boiling glacial acetic acid in sunlight. Dr. H. Müller finds that the formation of monochloracetic acid is facilitated by dissolving a little iodine in the hydrated acetic acid, and passing a stream of chlorine through the boiling solution. On submitting the products of this reaction to repeated distillation, a substance is obtained boiling at 186° C. (367° F.), and solidifying to a crystalline mass which melts at 64° C. (147° F.) and dissolves with facility in water. This acid, when heated with potash, is converted into potassium glycollate (p. 604):

$$\underset{\text{Chloracetic acid.}}{C_2H_3ClO_2} + 2KHO = KCl + \underset{\text{Potassium glycollate.}}{C_2H_3O_3K} + OH_2$$

Dichloracetic acid, $C_2HCl_2O(OH)$, is produced, together with the preceding compound, by the action of chlorine and iodine on boiling acetic acid, and is found in that portion of the product which boils above 188° C. (370° F.).

According to Maumené,* it may be obtained by exposing monochloracetic acid in large flasks to the action of dry chlorine (5 atoms of chlorine to 3 molecules of chloracetic acid) for twenty-four hours, warming the product to expel hydrochloric acid, and then distilling. At ordinary temperatures it is a liquid having a specific gravity of 1·5216 at 15° C. (59° F.), and boiling at 105° C. (221° F.). According to Müller, it remains liquid when cooled; but according to Maumene, it crystallizes in rhombohedral plates. It forms a soluble silver salt, $C_2HCl_2O_2Ag$, which is decomposed when its solution is heated with silver oxide to 75° or 80°, giving off a mixture of carbon monoxide and dioxide:

$$2C_2HCl_2O_2Ag + 3Ag_2O = 2CO + 2CO_2 + 4AgCl + 2Ag_2 + OH_2.$$

Trichloracetic acid, $C_2Cl_3O(OH)$.—Discovered by Dumas. When a small quantity of crystallizable acetic acid is introduced into a bottle of dry chlorine gas, and the whole exposed to the direct solar rays for several hours, the interior of the vessel is found coated with a white crystalline substance, which is a mixture of trichloracetic acid with a small quantity of oxalic acid. The liquid at the bottom contains the same substances, together with the unaltered acetic acid. Hydrochloric and carbonic acid gases are at the same time produced, together with a suffocating vapor, resembling carbonyl chloride. The crystalline matter is dissolved out by a small quantity of water added to the liquid contained in the bottle, and the whole is placed in the vacuum of the air-pump, with capsules containing fragments of caustic potash and concentrated sulphuric acid. The oxalic acid is first deposited, and afterward the trichloracetic acid, in beautiful rhombic crystals. If the liquid refuses to crystallize, it may be distilled with a little anhydrous phosphoric acid, and then evaporated. The crystals are spread upon bibulous paper to drain, and dried in a vacuum.

The reaction probably takes place according to the equation:

$$\underset{\text{Acetic acid.}}{4C_2H_4O_2} + 11Cl_2 = \underset{\text{Trichloracetic acid.}}{2C_2HCl_3O_2} + \underset{\text{Oxalic acid.}}{C_2H_2O_4} + 10HCl + \underset{\text{Chloroform.}}{2CHCl_3}$$

* Bull. Soc. Chim. de Paris, [2], i. 417.

The chloroform is converted, by the further action of the chlorine, into carbon tetrachloride, CCl_4 (Maumené).

Trichloracetic acid may also be produced synthetically, viz., by the action of chlorine and water on carbon tetrachloride, this compound first taking up 2 atoms of chlorine and forming carbon trichloride, C_2Cl_6, and the latter being converted by the water into hydrochloric and trichloracetic acids:

$$C_2Cl_6 + 2OH_2 = 3HCl + C_2HCl_3O_2$$

Trichloracetic acid is a colorless and extremely deliquescent substance: it has a faint odor, and sharp caustic taste, bleaching the tongue and destroying the skin; the solution is powerfully acid. At 46° C. (115° F.) it melts to a clear liquid, and at 199° C. (390° F.) boils and distils unchanged. The density of the fused acid is 1·617; that of the vapor, which is very irritating, is probably 5·6.

The *trichloracetates* are analogous to the acetates. The *potassium-salt*, $2C_2Cl_3O_2K$. aq., crystallizes in fibrous silky needles, permanent in the air. The *ammonium-salt*, $2C_2Cl_3O_2NH_4$. 5 Aq., is also crystallizable and neutral. The *silver-salt*, $C_2Cl_3O_2Ag$, is soluble, and crystallizes in small, grayish scales, easily altered by light.

Trichloracetic acid boiled with excess of ammonia yields ammonium carbonate and chloroform:

$$C_2HCl_3O_2 + 2NH_3 + OH_2 = CO_3(NH_4)_2 + CHCl_3$$

With caustic potash, it yields a smaller quantity of chloroform, together with potassium chloride, carbonate, and formate. The chloride and formate are secondary products of the reaction of the alkali upon the chloroform.

Nascent hydrogen reduces trichloracetic to acetic acid. When potassium or sodium amalgam is put into a strong aqueous solution of trichloracetic acid, the temperature of the liquid rises, without disengagement of gas, and the solution is found to contain acetate and chloride of potassium, together with caustic potash.

Bromacetic Acids.—*Monobromacetic acid*, $C_2H_2BrO(OH)$, discovered by Perkin and Duppa, is analogous in every respect to monochloracetic acid. It is formed by acting with bromine on glacial acetic acid in sealed tubes at a temperature above that of boiling water. Ammonia converts it into glycocine, $C_2H_5NO_2$ (p. 614).

Dibromacetic acid, $C_2HBr_2O(OH)$, is obtained by the further action of bromine upon bromacetic acid. It is a liquid boiling at 240° C. (464° F.); heated with silver oxide and water, it is decomposed into silver bromide and bromoglycollic acid:

$$\underset{\text{Dibromacetic acid.}}{2C_2H_2Br_2O_2} + Ag_2O + H_2O = 2AgBr + \underset{\text{Bromoglycollic acid.}}{2C_2H_3BrO_3}$$

Ethyl-dibromacetate, $C_2HBr_2O_2 . C_2H_5$, produced by heating an alcoholic solution of the acid in a sealed tube, is an oily liquid which is decomposed by ammonia, yielding alcohol and dibromacetamide:

$$C_2HBr_2O_2 . C_2H_5 + NH_3 = C_2H_5OH + NH_2C_2HBr_2O$$

Iodacetic Acid, $C_2H_3IO_2$, and Di-iodacetic Acid, $C_2H_2I_2O_2$, have likewise been obtained.

Thiacetic Acid, C_2H_4OS, or $C_2H_3O(SH)$, or $O{=}C(CH_3){-}SH$. — This acid, dis-

covered by Kekulé, is formed by the action of phosphorus pentasulphide on glacial acetic acid:

$$5C_2H_3O(OH) + P_2S_5 = P_2O_5 + 5C_2H_3O(SH)$$

Thiacetic acid is a colorless liquid, boiling at 93° C. (199° F.); it smells like acetic acid and hydrogen sulphide. With solution of lead acetate, it forms a crystalline precipitate containing $(C_2H_3O)_2Pb''S_2$, or $Pb''\begin{cases}SC_2H_3O\\SC_2H_3O\end{cases}$

Amidacetic Acid, or Glycocine, $C_2H_5NO_2$, or $C_2H_3(NH_2)O_2$.—This compound is formed by the action of ammonia on bromacetic or chloracetic acid:

$$\underset{\text{Chloracetic acid.}}{C_2H_3ClO_2} + 2NH_3 = NH_4Cl + \underset{\text{Amidacetic acid.}}{C_2H_3(NH_2)O_2}$$

It is also produced by the action of acids or alkalies upon animal substances, such as glue, hippuric acid, glycollic acid, etc. From hippuric acid it is formed according to the equation:

$$\underset{\text{Hippuric acid.}}{C_9H_9NO_3} + OH_2 = \underset{\text{Glycocine.}}{C_2H_5NO_2} + \underset{\text{Benzoic acid.}}{C_7H_6O_2}$$

To prepare it, hippuric acid is boiled for several hours with concentrated hydrochloric acid; the liquid is evaporated nearly to dryness; the residue exhausted with cold water; the solution treated with lead oxide, to separate the hydrochloric acid, and filtered: the filtrate, after precipitation of the lead by sulphuretted hydrogen, yields on evaporation hard transparent crystals of glycocine. Glycocine is easily soluble in water, nearly insoluble in alcohol and ether. It combines with acids in different proportions. With sulphuric acid it forms the compound $(C_2H_5NO_2)_2SO_4H_2$; and on addition of alcohol to a solution of this sulphate, a salt crystallizing in rectangular prisms is deposited, containing $3C_2H_5NO_2 . SO_4H_2$. Glycocine also forms saline compounds by substitution of metal for hydrogen; for example, $C_4H_8Cu''N_2O_4 . OH_2$, and $C_2H_4AgNO_2$: it also combines with metallic salts, forming crystalline compounds, such as $C_2H_5NO_2 . NO_3K$, and $C_2H_5NO_2 . NO_3Ag$.

Nitrous acid converts glycocine into glycollic or oxyacetic acid:

$$\underset{\text{Amidacetic acid.}}{C_2H_3(NH_2)O_2} + 2NO(OH) = \underset{\text{Oxyacetic acid.}}{C_2H_3(OH)O_2} + OH_2 + N_2$$

Methyl-glycocine, or *Sarcosine*, $C_3H_7NO_2$, or $C_2H_4(CH_3)NO_2$, isomeric with alanine (p. 619), is produced by digesting ethyl-chloracetate with an excess of a concentrated aqueous solution of methylamine:

$$C_2H_2ClO_2 . C_2H_5 + 2NH_2CH_3 + OH_2 = \underset{\text{Sarcosine.}}{C_2H_2(CH_3)(NH_2)O_2} + \underset{\text{Methylamine hydrochloride.}}{NH_2CH_3 . HCl} + \underset{\text{Alcohol.}}{C_2H_5(OH)}$$

The same compound is formed by boiling creatine * with baryta-water; ammonia is then eliminated, a precipitate of barium carbonate separates, and the solution, after the removal of the barium by carbonic acid, yields on evaporation colorless rhombic prisms of sarcosine. The creatine splits into sarcosine and urea, the latter being further decomposed into ammonia

* See the chapter on Organic Bases.

and carbonic acid. Sarcosine dissolves with facility in water; it is difficultly soluble in alcohol, insoluble in ether, and has no action upon vegetable colors. It combines with acids to soluble salts, which have an acid reaction. The double salt of sarcosine with platinum tetrachloride crystallizes in large yellow octohedrons having the composition $2C_3H_7NO_2 . 2HCl . PtCl_4 . 2\,Aq$.

Propionic Acid, $C_3H_6O_2 = C_3H_5O(OH) = \begin{matrix} C_2H_5 \\ | \\ COOH \end{matrix}$. — This acid is produced: 1. As a potassium-salt by the combination of carbon-dioxide with potassium-ethyl, $CO_2 + C_2H_5K = CO(C_2H_5)OK$. — 2. By the action of acids or alkalies on ethyl cyanide (p. 599). — 3. By the simultaneous action of water and carbonyl chloride on ethane (p. 599). — 4. By the oxidation of propionic aldehyde, C_3H_6O. It should also be formed by oxidation of normal propylic alcohol: but that compound is not known with certainty (p. 531). — 5. Together with acetic acid, by oxidizing propione, or metacetone, $C_5H_{10}O$, with aqueous chromic acid. This is the process by which it was first obtained. — 6. From lactic acid — from which it differs only by containing one atom of oxygen less — by the action of hydriodic acid:

$$\underset{\text{Lactic acid.}}{C_3H_6O_3} + 2HI = \underset{\text{Propionic acid.}}{C_3H_6O_2} + OH_2 + I_2$$

7. Together with several other products, in the fermentation of glycerin, and likewise of sugar, by the action of putrid cheese in presence of calcium carbonate.

Propionic acid is usually prepared by the second of the above-mentioned processes. Ethyl cyanide is added by drops to a moderately strong solution of potash heated in a tubulated retort, the distillate being repeatedly poured back as long as it smells of ethyl cyanide. The residue in the retort, consisting of potassium propionate, is then evaporated down to dryness, and distilled with syrupy phosphoric acid.

Propionic acid, when perfectly dry, crystallizes in laminæ, and boils at 140° C. (284° F.). It is soluble in water, and when the water is quite saturated with it, the excess of acid floats on the surface in the form of an oil. It has a very sour taste, and a somewhat pungent odor.

The propionates are soluble in water. The *barium-salt*, $(C_3H_5O_2)_2Ba''$, yields propione by dry distillation.

Propionic acid forms substitution-products with chlorine, bromine, and iodine. *Chloropropionic acid*, $C_3H_5ClO_2$, does not appear to be formed by the action of chlorine on propionic acid; but it is obtained by treating the calcium salt of lactic acid with phosphorus pentachloride, whereby lactyl chloride or chloropropionyl chloride is formed, and decomposing this chloride with water:

$$\underset{\text{Lactic acid.}}{C_3H_4O(OH)_2} + PCl_5 = \underset{\substack{\text{Chloropropionyl} \\ \text{chloride.}}}{C_3H_4ClO . Cl} + PCl_3O + OH_2$$

$$\underset{\substack{\text{Chloropropionyl} \\ \text{chloride.}}}{C_3H_4ClO . Cl} + OH_2 = HCl + \underset{\substack{\text{Chloropropionic} \\ \text{acid.}}}{C_3H_4ClO(OH)}$$

Chloropropionic acid is a liquid less volatile than propionic acid, and having the odor of trichloracetic acid. Nascent hydrogen converts it into propionic acid.

Bromopropionic acid, $C_3H_5BrO_2$, produced by the action of bromine on propionic acid, is converted by alcoholic ammonia into *alanine*, or *amidopropianic acid:*

$$C_3H_5BrO_2 + 2NH_3 = C_3H_5(NH_2)O_2 + NH_4Br.$$

Alanine, homologous with glycocine and isomeric with sarcosine (p. 614), is also produced by boiling a mixture of aldehyde-ammonia and hydrocyanic acid with dilute hydrochloric acid:

$$\underset{\text{Aldehyde-ammonia.}}{C_2H_4O.NH_3} + CNH + HCl + OH_2 = NH_4Cl + \underset{\text{Alanine.}}{C_3H_7NO_2}.$$

On evaporating the solution, extracting the hydrochloride of alanine with alcohol, and separating the hydrochloric acid by hydrated lead oxide, a solution is obtained containing alanine in combination with lead oxide, from which the alanine may be separated by saturating the solution with sulphuretted hydrogen, filtering, and evaporating. It forms rhombic prisms of a pearly lustre, easily soluble in alcohol, sparingly soluble in ether. Alanine, like glycocine, combines with acids, bases, and salts.

Nitrous acid converts alanine into lactic or oxypropionic acid, $C_4H_6O_3$, the reaction being exactly similar to that by which glycocine is converted into glycollic acid.

Butyric Acid, $C_4H_8O_2 = C_4H_7O(OH)$. — Acids having this composition, are obtained by the following synthetical processes:

a. By the action of ethyl-iodide on monosodic ethyl acetate (p. 600), and decomposition of the resulting ethylic ethyl-acetate with potash: the product thus obtained is ethyl-acetic or normal butyric acid:

$$\underset{\substack{\text{Monosodic}\\ \text{ethyl-acetate.}}}{\begin{matrix}CH_2Na\\ |\\ COOC_2H_5\end{matrix}} + \underset{\substack{\text{Ethyl}\\ \text{iodide.}}}{C_2H_5I} = NaI + \underset{\substack{\text{Ethylic}\\ \text{ethyl-acetate.}}}{\begin{matrix}CH_2C_2H_5\\ |\\ COOC_2H_5\end{matrix}}$$

$$\underset{\substack{\text{Ethylic}\\ \text{ethyl-acetate.}}}{\begin{matrix}CH_2C_2H_5\\ |\\ COOC_2H_5\end{matrix}} + \underset{\substack{\text{Water.}}}{HOH} = \underset{\substack{\text{Ethyl}\\ \text{alcohol.}}}{C_2H_5(OH)} + \underset{\substack{\text{Ethylacetic}\\ \text{acid.}}}{\begin{matrix}CH_2C_2H_5\\ |\\ COOH\end{matrix}}$$

β. Disodic ethyl-acetate, treated in like manner with methyl-iodide, yields dimethylic ethyl-acetate:

$$\begin{matrix}CHNa_2\\ |\\ COOC_2H_5\end{matrix} + 2CH_3I = 2NaI + \begin{matrix}CH(CH_3)_2\\ |\\ COOC_2H_5\end{matrix};$$

and this compound, treated with potash, is converted into dimethyl-acetic or isobutyric acid, $\begin{matrix}CH(CH_3)_2\\ |\\ COOH.\end{matrix}$

Ethylacetic acid boils at 161° C. (322° F.), dimethylacetic acid at 152° C. (305° F.) (Frankland and Duppa).

Butyric acid, identical with the first of these synthetical products, occurs ready-formed in tamarinds and a few other plants, and in certain beetles, and is obtained artificially by several processes.

1. By oxidation of primary butyl alcohol.* — 2. By saponification of ordinary butter, which contains tributyrin:

$$\underset{\text{Tributyrin.}}{(C_3H_5)'''(OC_4H_7O)_3} + 3KOH = \underset{\substack{\text{Potassium}\\ \text{butyrate.}}}{3C_4H_7OH} + \underset{\text{Glycerin.}}{C_3H_5(OH_3)}$$

* If Erlenmeyer's view of the constitution of the fermentation alcohols be correct, the acid produced by oxidation of butyl alcohol obtained from fusel oil, should be isobutyric acid: the point requires further investigation.

Other acids of the series are, however, formed at the same time, which are difficult to separate.

3. By the fermentation of sugar in contact with putrid cheese and chalk, calcium lactate being first formed in large quantity, and afterward dissolved and converted into butyrate, which may be decomposed by sulphuric acid, and distilled. The conversion of lactic into butyric acid probably takes place as shown by the equation:

$$\underset{\text{Lactic acid.}}{2C_3H_6O_3} = \underset{\text{Butyric acid.}}{C_4H_8O_2} + 2CO_2 + 2H_2$$

Butyric acid thus obtained is a colorless, very mobile liquid, having an odor of acetic acid and also of rancid butter. Its specific gravity is 0·9886 at 0°, and 0·9739 at 15°. At the temperature of a mixture of solid carbonic acid and ether it crystallizes in large laminæ. It boils at 164° C. (327° F.), giving off a vapor which burns with a blue flame. It dissolves in all proportions in water, alcohol, and wood-spirit. Boiling nitric acid converts it into succinic acid:

$$\underset{\substack{\text{Butyric}\\\text{acid.}}}{2C_4H_8O_2} + O_6 = 2OH_2 + \underset{\substack{\text{Succinic}\\\text{acid.}}}{2C_4H_6O_3}$$

The metallic butyrates are, for the most part, soluble in water, and crystallizable. The *calcium salt* $C_4H_7O_2Ca''$, yields butyrone, $C_4H_7O.C_3H_7$, by dry distillation.

Ethyl Butyrate, $C_4H_7O_2.C_2H_5$, is a liquid having a pleasant fruity odor: it is sometimes used for flavoring confectionery.

Butyric acid, subjected to the action of dry *chlorine*, is converted first into *dichlorobutyric acid*, $C_4H_6Cl_2O_2$, and afterward into *tetrachlorobutyric acid*, $C_4H_4Cl_4O_2$. Heated with *bromine* in sealed tubes to 150°–200° C. (302°–392° F.), it forms *mono-* or *dibromobutyric acid*, according to the proportions used. Dibromobutyric acid is crystallizable.

Amidobutyric acid, $C_4H_9NO_2$, or $C_4H_7(NH_2)O_2$, is said to exist, together with its homologue, leucine or amidocaproic acid, in the pancreas of the ox.

Valeric, or Valerianic Acid, $C_5H_{10}O_2 = C_5H_9O(OH)$.—This acid occurs in valerian root, in angelica root, in the berries of the guelder rose (*Viburnum opulus*), and probably in many other plants. It is produced by the oxidation of amyl alcohol, either by absorption of atmospheric oxygen under the influence of platinum black, or by treatment with aqueous chromic acid, or by heating it with a mixture of caustic potash and quicklime, the reaction, in this last case, being attended with evolution of hydrogen:

$$\underset{\substack{\text{Amyl}\\\text{alcohol.}}}{C_5H_{12}O} + KOH = \underset{\substack{\text{Potassium}\\\text{valerate.}}}{C_5H_9O_2K} + OH_2 + H_2$$

The potassium salt, distilled with sulphuric acid, yields valeric acid.

The most advantageous mode of preparing valeric acid, is to oxidize amyl alcohol with a mixture of sulphuric and potassium bichromate. 4 parts of the bichromate in powder, 6 parts of oil of vitriol, and 8 parts of water are mixed in a capacious retort, and 1 part of amyl alcohol is added by small portions, with strong agitation, the retort being plunged into cold water to moderate the violence of the reaction. When the change appears complete, the deep-green liquid is distilled nearly to dryness, the product mixed with excess of caustic potash, and the aqueous solution separated mechanically from a pungent, colorless, oily liquid which floats upon it, consisting of amyl valerate. The alkaline solution is then evaporated to a

small bulk, and decomposed by dilute sulphuric acid in excess. The greater part of the valeric acid then separates as an oily liquid lighter than water: this is a hydrate consisting of $C_5H_{10}O_2 . OH_2$. When distilled alone, it undergoes decomposition: water, with a little of the acid, first appears, and eventually the pure acid, $C_5H_{10}O_2$, in the form of a thin, mobile, colorless oil, having the persistent and characteristic odor of valerian root. It has a sharp and acid taste, reddens litmus strongly, bleaches the tongue, and burns when inflamed with a bright, yet smoky light. Valeric acid has a density of 0·937: it boils at 175° C. (347° F.). Placed in contact with water, it absorbs a certain quantity, and is itself to a certain extent soluble.

Valeric acid is active or inactive to polarized light, accordingly as it has been prepared from active or inactive amyl alcohol. That which has been prepared from the active alcohol produces a right-handed rotation of 43° in a tube 50 centimetres long.*

The metallic valerates are not of much importance; several of them are crystallizable. The *silver-salt* contains $C_5H_9O_2Ag$. A solution of potassium valerate, subjected to electrolysis, yields dibutyl, C_8H_{18} (p. 475).

Ethyl valerate, $C_5H_9O_2 . C_2H_5$, is obtained by passing hydrochloric acid gas into an alcoholic solution of valeric acid. Ammonia converts it into valeramide, $C_5H_9ONH_2$.

Chlorovaleric Acids.—*Trichlorovaleric acid*, $C_5H_7Cl_3O_2$, obtained by the prolonged action of chlorine on valeric acid in the dark, aided toward the end of the process by a gentle heat, is an oily liquid, becoming very viscid at 18° C. (64° F.), perfectly mobile at 30° C. (86° F.). In contact with water it forms a very viscid hydrate, which sinks to the bottom. It dissolves in aqueous alkalies, and is precipitated by acids in its original state.

Tetrachlorovaleric acid, $C_5H_6Cl_4O_2$, is the ultimate product of the action of chlorine on the preceding substance, aided by exposure to the sun. It is a semifluid, colorless oil, destitute of odor, of powerful pungent taste, and heavier than water. It can neither be solidified by cold nor distilled without decomposition. In contact with water, it forms a hydrate containing $C_5H_6Cl_4O_2 . OH_2$, which is slightly soluble in water, easily soluble in alcohol and ether.

Isomeric forms of Valeric acid. — The formula $C_5H_{10}O_2$ may include the four following compounds:

$CH_2CH_2CH_2CH_3$	$CH_2CH(CH_3)_2$	$CHCH_3[CH_2CH_3]$	$C(CH_3)_3$
COOH	COOH	COOH	COOH
Propyl-acetic acid.	Isopropyl-acetic acid.	Methyl-ethyl-acetic acid.	Trimethyl acetic acid.

The second and fourth of these acids have been prepared by Frankland and Duppa.†

Ethyl isopropylacetate, $\begin{matrix} CH_2CH(CH_3)_2 \\ | \\ COOC_2H_5 \end{matrix}$, is obtained by the action of isopropyliodide, $CH(CH_3)_2I$, on monosodic ethyl acetate, and from this ether *isopropylacetic acid* is prepared, as in the similar cases previously described. It is identical in every respect with valeric acid prepared from optically inactive amyl alcohol.

Trimethylacetic acid is obtained as an ethyl ether by the action of methyl iodide on trisodic ethyl acetate:

* *Pedler*, Chem. Soc. Journal [2], vi. 74. † Chem. Soc. Journal [2], v. 102.

$$\begin{matrix}CNa_3\\|\\COOC_2H_5\end{matrix} + 3CH_3I = 3NaI + \begin{matrix}C(CH_3)_3\\|\\COOC_2H_5\end{matrix}$$

Caproic Acid, $C_6H_{12}O_2 = C_6H_{11}O(OH) = \begin{matrix}C_5H_{11}\\|\\COOH\end{matrix}$.—This acid is produced by the action of alkalies or acids on amyl cyanide, $C_5H_{11}CN$ (p. 599); also, as a sodium-salt, by the action of carbon dioxide on sodium-amyl: $CO_2+C_5H_{11}Na=CO(C_5H_{11})ONa$.* It occurs as a glyceride in the butter of cow's milk, and abundantly in cocoa-nut oil; it is a not unfrequent product of the oxidation of fatty acids of higher atomic weight, and is also produced by the oxidation of poppy oil and of casein. It may be prepared from cocoa-nut oil by saponifying the oil with strong soda-lye, and distilling the soap with dilute sulphuric acid. The distillate contains caproic and caprylic acids, and, when neutralized with baryta and evaporated, yields, first crystals of barium caprylate, and afterwards verucose crystals of the caproate, which, when decomposed by sulphuric acid, yield caproic acid.

Caproic acid is a clear mobile oil of sp. gr. 0·931 at 15°, having a sudorific odor and pungent taste. The acid prepared from amyl cyanide solidifies at —9° C. (16° F.), boils at 198° C. (388° F.), and is active to polarized light. That from cocoa-nut oil boils between 202° and 209° C. (395°–408° F.) (perhaps owing to admixture of caprylic acid), and is optically inactive.

The metallic caproates are soluble and crystallizable. A strong solution of the potassium-salt, subjected to electrolysis, yields diamyl, $C_{10}H_{22}$ (p. 475). The silver-salt, $C_6H_{11}O_2Ag$, is nearly insoluble in water, and crystallizes in broad plates, but is little altered by exposure to light.

Diethyl-acetic Acid, $\begin{matrix}CH(C_2H_5)_2\\|\\COOH\end{matrix}$, the ethylic ether of which is prepared by the action of ethyl iodide on disodic ethyl acetate, is isomeric with caproic acid. It has a different odor, and its silver-salt forms silky asbestos-like crystals, soluble in water, and turning brown when exposed to a strong light.

Amidocaproic Acid, or Leucine, $C_6H_{13}NO_2$ or $C_6H_{11}(NH_2)O_2$, has not been obtained directly from any derivative of caproic acid, but is produced by digesting together valeral-ammonia, hydrocyanic acid, and hydrochloric acid, the reaction being analogous to that by which alanine is prepared from the ammonia-compound of acetic aldehyde:

$$\underset{\text{Valeral-ammonia.}}{C_5H_{10}O.NH_3} + CNH + HCl + OH_2 = \underset{\text{Leucine.}}{C_6H_{13}NO_2} + NH_4Cl$$

Leucine is also formed by the decomposition of animal substances, such as glue, horn, wool, &c., during putrefaction, and by the treatment of these substances with acids or alkalies. It was first discovered in putrid cheese; more recently it has been found in several parts of the animal organism. Leucine crystallizes in white shining scales, which melt at 100°, and may be sublimed without decomposition; it is but little soluble in water, still less in alcohol, insoluble in ether. When heated with caustic baryta, it splits into carbon dioxide and amylamine: $C_6H_{13}NO_2=C_5H_{13}N+CO_2$. It unites with acids, bases, and salts. Treatment with nitrous acid converts it into leucic acid, $C_6H_{12}O_3$, homologous with lactic and glycollic acids.

Œnanthylic Acid, $C_7H_{14}O_2 = C_7H_{13}(OH) = \begin{matrix}C_6H_{13}\\|\\COOH\end{matrix}$.— This acid is produced

* Wanklyn and Schenk, Chem. Soc. Journal [2], vi. 31.

from œnanthol, or œnanthylic aldehyde, $C_7H_{14}O$ (a liquid obtained by the dry distillation of castor-oil), by oxidation in the air, or with nitric acid, or with chromic acid; also by oxidation of castor-oil with nitric acid. *Amyl-acetic acid*, isomeric or identical with it, is obtained as an ethylic ether, together with several other products, by the action of amyl iodide on disodic ethyl acetate.

Œnanthylic acid is a transparent colorless oil, having an unpleasant odor like that of codfish. It boils, according to Strecker, at 212° C. (413° F.). It is insoluble in water, but soluble in alcohol and ether. When heated with baryta, it gives off sextane or hexyl hydride, C_6H_{14}, the baryta abstracting carbon dioxide: $C_7H_{14}O_2 = CO_2 + C_6H_{14}$. The potassium-salt, subjected to electrolysis, yields *dihexyl*, $C_{12}H_{26}$.

Caprylic Acid, $C_8H_{16}O_2 = C_8H_{15}O(OH)$, occurs as a glyceride in the butter of cow's-milk and in cocoa-nut oil; it is also found in several kinds of fusel-oil, partly free, partly as an ethylic or amylic ether. It is best prepared by saponification of cocoa-nut oil; its barium-salt, being very sparingly soluble, is easily separated from the barium-salt of caproic acid formed at the same time.

Caprylic acid has a faint but unpleasant odor, especially when warmed. It solidifies at 12° C. (54° F.), melts at 15° C. (59° F.), and boils at 236°–238° C. (457°–460° F.). When boiled with nitric acid, it is converted into nitrocaprylic acid, $C_8H_{15}(NO_2)O_2$.

Pelargonic Acid, $C_9H_{18}O_2 = C_9H_{17}(OH)$, was first obtained from the leaves of the geranium (*Pelargonium roseum*), in which it exists ready formed. It may be procured in large quantity by the action of nitric acid upon the essential oil of rue (which contains the two aldehydes, $C_{11}H_{22}O$ and $C_{12}H_{24}O$); also, together with several acids of the fatty series, by the action of boiling nitric acid on oleic acid. It is a liquid having a slightly unpleasant odor, and boiling at 260° C. (500° F.).

Ethyl pelargonate, $C_9H_9O_2 . C_2H_5$, may be easily produced by dissolving the acid in strong alcohol, and passing a current of hydrochloric acid through the solution. It is a liquid of specific gravity 0·862, and boiling at 250° C. (482° F.). It has a powerful and most intoxicating vinous odor.

The aroma possessed by certain wines appears to be due to the presence of the ether of pelargonic acid, which, in this case, is probably generated during fermentation. When such wines, or the residues of their fermentation, are distilled on the large scale, an oily liquid passes over towards the close of the operation, which consists, in great measure, of the crude ether: it may be purified by agitation with solution of potassium carbonate, freed from water by a few fragments of calcium chloride, and redistilled. The pelargonic ether obtained by this process was originally described as *œnanthic ether*, and the acid as *œnanthic acid*.

Rutic or **Capric Acid**, $C_{10}H_{20}O_2$.—This acid exists as a glyceride in ordinary butter and in cocoa-nut oil: it occurs also in several kinds of fusel-oil, and is formed by the oxidation of oleic acid and of oil of rue. It may be obtained pure and in tolerable quantity from the liquid which remains in the distillation of the fusel-oil of the Scotch distilleries (p. 626) after the amyl alcohol has been distilled off at 132° C. (270° F.). This residue consists chiefly of amyl rutate, $C_{10}H_{19}O_2 . C_5H_{11}$, and when distilled with potash gives off amyl alcohol and leaves potassium rutate, from which the rutic acid may be obtained by distillation with sulphuric acid.

Rutic acid is a colorless crystalline body, having a slight odor of the goat, becoming stronger when the acid is warmed. It melts at 27°–30° C. (80°–86° F.), is very soluble in cold alcohol and ether, insoluble in cold water, slightly soluble in boiling water, and dissolves without alteration in strong nitric acid.

The metallic rutates are mostly sparingly soluble in water. The barium-salt, $(C_{10}H_{19}O_2)_2Ba''$, separates from solution in boiling water in needle-shaped or large prismatic crystals which float on the water if not moistened.

Lauric Acid, $C_{12}H_{24}O_2$, occurs as a glyceride (laurostearin) in the fat of the bay-tree (*Laurus nobilis*), and in the solid fat and volatile oil of pichurim beans (*Fabæ Pichurim maj.*). It is prepared by saponifying these fats with caustic alkali, and decomposing the resulting soap with tartaric or hydrochloric acid. It likewise occurs, together with other fatty acids, or their glycerides, in cocoa-nut oil and the oils or fats of several other plants, also in spermaceti; and is separated from the mixtures of fatty acids resulting from the saponification of these substances by a complicated process of fractional precipitation with barium and magnesium salts, into the details of which we cannot enter.*

Lauric acid is insoluble in water, but dissolves easily in alcohol and ether, and crystallizes from alcohol in white, silky needles, which melt at about 43° C. (109° F.).

The laurates of the alkali-metals and of barium are soluble in water; the other salts are insoluble or sparingly soluble. The *calcium salt*, $(C_{12}H_{23}O)_2Ca''$, is resolved by distillation into calcium carbonate and laurostearone:

$(C_{12}H_{23}O)_2Ca''$	=	CO_3Ca''	+	$C_{24}H_{46}O$
Calcium laurate.		Calcium carbonate.		Lauro-stearone.

Myristic Acid, $C_{14}H_{28}O_2$.—This acid occurs as a glyceride in nutmeg-butter and Otoba fat; also, together with lauric acid, in Dika bread, the fruit of *Mangifera gabonensis*, an African tree; and, together with other fatty acids, in cocoa-nut oil and spermaceti. It may be produced from crude ethal (cetyl alcohol) by heating with a mixture of potash and lime, its formation being doubtless due to the presence of methal or myristic alcohol in the crude ethal (p. 543):

$C_{14}H_{30}O$	+	KHO	=	$C_{14}H_{27}O_2K$	+	$2H_2$
Methal.				Potassium myristate.		

Lauric acid is likewise produced by a similar process from crude ethal, doubtless because that substance also contains lethal or lauric alcohol, $C_{12}H_{26}O$.

Pure myristic acid is most easily obtained by saponification of Otoba fat (from *Myristica Otoba*). It forms white, shining, crystalline laminæ, melting at 53·8° C. (129° F.). It is quite insoluble in water and in ether, but dissolves easily in hot alcohol, and crystallizes therefrom on cooling.

The myristates of the alkali-metals, $C_{14}H_{27}O_2K$, &c., are soluble in water, and not decomposed thereby (like the stearates). The other myristates are insoluble or sparingly soluble, and are obtained by precipitation.

Myristic oxide, or *Anhydride*, $(C_{14}H_{27}O)_2O$, is obtained, like other acid oxides of the series, by the action of phosphorus oxychloride on potassium myristate. It is a fatty substance, having a somewhat lower melting point than myristic acid. It is slowly saponified by boiling caustic potash.

Myristin, $(C_3H_5)'''(C_{14}H_{29}O_2)_3$, the glyceride of myristic acid, is obtained by pressing nutmegs between hot plates, exhausting the crude fat thus obtained with spirits of wine, and crystallizing the undissolved portion from boiling ether. It is a crystalline fat having a silky lustre.

Palmitic Acid, $C_{16}H_{32}O_2$.—This acid occurs as a glyceride (tripalmitin) in many natural fats, often associated with stearin. Palm-oil, the produce of

* See Watts's Dictionary of Chemistry, vol. iii. p. 474.

Elais guianensis, Chinese tallow, the produce of the tallow-tree (*Stillingia sebifera*), and Japan wax, from *Rhus succedania*, consist mainly of tripalmitin. Palmitic acid is easily prepared by saponifying palm-oil with caustic potash, decomposing the soap with sulphuric acid, and crystallizing the separated fatty acid several times from hot alcohol till it exhibits a constant melting point. Chinese tallow may be saponified with alcoholic potash, and Japan wax by fusion with solid potassium hydrate, and the soap treated in a similar manner.

Palmitic acid exists also as cetyl palmitate (cetin), $C_{16}H_{31}O_2 \cdot C_{16}H_{33}$, in spermaceti, and as myricyl palmitate (melissin), $C_{16}H_{31}O_2 \cdot C_{30}H_{61}$, in bees'-wax. It is produced, together with acetic acid, by melting oleic acid with potassium hydrate:

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + 2KOH = \underset{\text{Palmitic acid.}}{C_{16}H_{31}O_2K} + \underset{\text{Acetic acid.}}{C_2H_3O_2K} + H_2$$

Palmitic acid is a colorless, solid body without taste or smell, lighter than water. It is insoluble in water, but dissolves abundantly in boiling alcohol or ether. The solutions are acid, and when concentrated, solidify in a mass on cooling. When dilute they yield the acid in tufts of slender needles. It melts at 62° C. (144° F.), and solidifies on cooling in a mass of shining nacreous laminæ. When heated in a dish, it boils and evaporates without residue, and may be distilled almost without change. When gently heated in the air, it is but slightly altered, but at higher temperatures it takes fire, and burns with a bright smoky flame like other fats. It is attacked by chlorine at 100°, giving off hydrochloric acid, and forming oily substitution-products. Heated with alcohols, it forms compound ethers.

Palmitic acid forms normal or neutral salts, having the composition $C_{16}H_{31}O_2M$ for univalent, and $(C_{16}H_{31}O_2)_2M''$ for bivalent metals, and with the alkali-metals also, acid salts analogous to the acid acetates. The normal palmitates of potassium and sodium are soluble in water and alcohol; the rest are insoluble, and are obtained by precipitating a metallic salt with an alcoholic solution of sodium or potassium palmitate. The *normal potassium-salt*, $C_{16}H_{31}O_2K$, obtained by melting the acid with potassium carbonate, and exhausting with boiling alcohol, crystallizes in pearly scales. The *acid salt*, $C_{16}H_{31}O_2K \cdot C_{16}H_{32}O_2$, is precipitated on mixing a solution of 1 part of the normal salt in 20 parts of boiling water with 1000 parts of cold water. The *barium-salt*, $(C_{16}H_{31}O_2)_2Ba''$, is a white, pearly, crystalline powder; the *magnesium-salt*, $(C_{16}H_{31}O_2)_2Mg''$, is a snow-white, loose, crystalline precipitate.

Ethyl palmitate, $C_{16}H_{31}O_2 \cdot C_2H_5$, obtained by passing hydrochloric acid gas into a saturated alcoholic solution of palmitic acid, crystallizes in prisms, and melts at 24° C. (75° F.).

Glyceryl palmitates, or *Palmitins*. — There are three of these ethers—viz., *monopalmitin*, $(C_3H_5)'''(OH)_2(C_{16}H_{31}O_2)$, *dipalmitin*, $(C_3H_5)'''(OH)(C_{16}H_{31}O_2)_2$, and *tripalmitin*, $(C_3H_5)'''(C_{16}H_{31}O_2)_3$. The first and second are obtained by heating palmitic acid with glycerin in sealed tubes; the third by heating a mixture of 1 part of monopalmitin and 10 parts of palmitic acid to 250° C. (482° F.) for twenty-eight hours. They are all crystalline fats. Tripalmitin thus obtained melts at 46° C. (115° F.). Natural palmitin, obtained from palm-oil and other fats, has the composition of tripalmitin, but exhibits three isomeric (or rather allotropic) modifications (like those of stearin), melting respectively at 46°, 61·7°, and 62·8° C. (115°, 142°, 144° F.): the first appears to be identical with artificial tripalmitin.

Palm-oil comes chiefly from the coast of Africa. It has, when fresh, a deep orange-red tint, and a very agreeable odor: the coloring matter —

the nature of which is unknown — is easily destroyed by exposure to light, especially at a high temperature, and also by oxidizing agents. The oil melts at 27° C. (80° F.). By cautious pressure it may be separated into fluid olein and solid palmitin, which, when purified by crystallization from hot ether, is perfectly white. By keeping, palm-oil seems to suffer a change similar to that produced by saponification: in this state it is found to contain traces of glycerin and a considerable quantity of oleic acid, together with palmitic acid. The oil becomes harder and rancid, and its melting point is raised at the same time.

Margaric Acid, $C_{17}H_{34}O_2$. — This name was formerly applied to an acid, intermediate between stearic and palmitic acids, supposed to be produced, together with others, by the saponification of natural fats; but it is now restricted, for reasons to be presently mentioned, to an acid prepared by a definite reaction — viz., by the action of boiling alcoholic potash on cetyl cyanide:

$C_{16}H_{33}CN$	+	KOH	+	OH_2	=	NH_3	+	$C_{17}H_{33}O_2K$
Cetyl cyanide.								Potassium margarate.

The solid potassium salt thus obtained is decomposed by boiling dilute hydrochloric acid, and the separated margaric acid is purified by precipitating its ammoniacal solution with barium chloride, decomposing the precipitate with hydrochloric acid and ether, separating the ethereal solution by means of a pipette, and distilling off the ether. It forms white crystals, melting at 59·9° C. (140° F.), and is intermediate in all its properties between palmitic and stearic acids.

The so-called margaric acid, obtained by the saponification of natural fats, and regarded by Chevreul * and many other chemists as a distinct acid having the composition $C_{17}H_{34}O_2$, has been shown by Heintz † to be a mixture, resolvable into stearic acid and other fatty acids of lower melting points, chiefly palmitic acid. Such mixtures of solid fatty acids, or of the corresponding glycerides, cannot be completely resolved into their constituent fats by crystallization from alcohol, ether, or other solvents, which was the method of separation resorted to in the earlier investigations. The only effectual method of separation is to subject the alcoholic solution of the acids to a series of fractional precipitations with acetate of lead, barium, or magnesium, the stearate then separating out first.

Stearic Acid, $C_{18}H_{36}O_2$.—This acid was discovered by Chevreul as a constituent of the more solid fats of the animal kingdom. It is most abundant in these, especially in beef- and mutton-suet; but exists also, together with palmitic, myristic acid, &c., in the softer fats, such as the butter of cow's-milk, human fat, that of the goose, of serpents, of cantharides, and in spermaceti. It occurs also in vegetable fats, especially those of cacao-beans, of the berries of *Cocculus indicus*, and in shea-butter, obtained from the nuts of *Bassia Parkii*, a tree growing in West Africa. In all these fats it occurs as a glyceride, but in that of cocculus grains also in the free state.

Stearic acid is prepared from *beef-* or *mutton-suet*, or better from *cacao-fat*, by saponifying the fat with soda-lye, heating the soap-paste with water and dilute sulphuric acid, removing the separated fatty acids after cooling, washing them with water, and then dissolving them in as small a quantity as possible of hot alcohol. On cooling, the greater part of the solid acid separates out, while the oleic acid remains in solution, and may be sepa-

* *Recherches sur les corps gras d'origine animale.* Paris, 1823.

† For references to Heintz's memoirs, see Gmelin's Handbook, vol. xvi. p. 343.

rated by subjecting the mass, after draining, to strong pressure, redissolving the residue in a small quantity of alcohol, leaving it to separate by cooling, and again pressing the solid mass. From the mixture of solid fatty acids thus obtained, the stearic may be separated, in a comparatively pure state, by repeated crystallization from considerable quantities of alcohol, only the portion which first separates being each time collected. But to obtain pure stearic acid, it is better to dissolve the impure stearic acid (4 parts), melting at about 60° C. (140° F.), in such a quantity of hot alcohol that nothing will separate out on cooling, even to 0°, and mix the hot liquid with a boiling alcoholic solution of magnesium acetate (1 part). The magnesium-salt which separates on cooling, is pressed and boiled for some time with a large quantity of dilute hydrochloric acid, and the stearic acid thereby separated is repeatedly crystallized from alcohol, till it melts constantly at 69° to 70° C. (156°–158° F.).

Stearic acid is also easily prepared from the fat of cocculus-berries, which consists mainly of stearin, by saponifying it with potash, &c. According to Buff and Oudemanns,* the best material for the preparation of stearic acid is *shea-butter*, which contains about 70 per cent. stearic, and 30 per cent. oleic acid, but no other solid fatty acid.

On the large scale, impure stearic acid is prepared for the manufacture of stearin-candles, by saponifying some of the harder fats, generally with lime. The resulting lime-soap, decomposed by sulphuric acid, yields a mixture of fatty acids, which are pressed, first in the cold, and afterwards at a higher temperature, in order to separate the oleic acid from the less fusible palmitic and stearic acids. Another method, applied chiefly to palm-oil, consists in decomposing the fat with superheated steam, as described under GLYCERIN (p. 567). A third method consists in treating the fat with sulphuric acid, and distilling the product.

Pure stearic acid crystallizes from alcohol in nacreous laminæ or needles; it is tasteless and inodorous, and has a distinct acid reaction. At low temperatures it is heavier than water, having a specific gravity of 1·01 at 0°; but between 9° and 10° C. (48°–50° F.), its specific gravity is the same as that of water. It melts at 69°–69·2° C. (156° F.) to a colorless oil, which on cooling solidifies to a white, fine, scaly, crystalline mass, lamino-crystalline on the fractured surface. When heated it distils, for the most part, without alteration. *Chlorine* converts it into chlorostearic acid, $C_{18}H_{35}ClO_2$. Heated with *bromine* and water in a sealed tube, it is converted into bromostearic acid, $C_{18}H_{35}BrO_2$, and dibromostearic acid, $C_{18}H_{34}Br_2O_2$.

Stearates.—Stearic acid dissolves in a cold, aqueous solution of alkaline carbonate, probably from formation of acid carbonate, and does not expel the carbonic acid and form a mono-acid salt, till heated to about 100°. On the other hand, the stearates are decomposed by most other acids, the separated stearic acid rising to the surface as an oil when the liquid is warm. The stearates have the consistence of hard soaps and plasters, and are mostly insoluble in water. The *normal potassium-salt*, $C_{18}H_{35}O_2K$, separates on cooling from a solution of 1 part stearic acid and 1 part potassium hydrate in 10 parts of water, in white opaque granules. The *acid salt*, $C_{18}H_{35}O_2K \cdot C_{18}H_{36}O_2$, is obtained by decomposing the normal salt with 1000 parts or more of water, and separates in silvery scales from solution in boiling alcohol. *Normal sodium stearate*, $C_{18}H_{35}O_2Na$, is very much like the potassium-salt, but harder. The acid salt, $C_{18}H_{35}O_2Na \cdot C_{18}H_{36}O_2$, obtained by decomposing the normal salt with 2000 parts or more of water, separates from the hot solution in nacreous laminæ. The stearates of the earth-metals and heavy metals are insoluble in water, and are obtained by precipitation.

* Journal für praktische Chemie, lxxxix. 215.

Soaps consist of mixtures of the sodium or potassium-salts of stearic, palmitic, oleic, and other fatty or oily acids, and are produced by saponifying tallow, olive oil, and other fats with caustic alkalies. The soda-soaps are called *hard soaps:* they separate from the alkaline liquor, on addition of common salt, in hard, unctuous masses, which are the soaps in common use: this mode of separation is called *salting out.* The potash soaps, on the other hand, cannot be thus separated; for on adding salt to their solution, they are decomposed and converted into soda-soaps; but they are obtained in a semi-solid state by evaporating the solution. The products, called *soft soap*, always contain a considerable excess of alkali, and are used for cleansing and scouring when a powerful detergent is required.

Stearic ethers are formed by heating stearic acid with alcohols, monatomic or polyatomic. *Ethyl stearate*, $C_{18}H_{35}O_2..C_2H_5$, is most easily obtained by passing hydrochloric acid gas into an alcoholic solution of stearic acid. It resembles white wax, is inodorous and tasteless, melts at 30° C. (86° F.), and cannot be distilled without decomposition. It is readily decomposed by boiling with caustic alkalies. There are three *glyceryl stearates* or *stearins*, analogous in composition to the palmitins: *Monostearin*, $(C_3H_5)'''(OH)(C_{18}H_{35}O_2)$, prepared by heating a mixture of equal parts of stearic acid and glycerin to 200° C. (392° F.), in a sealed tube for 36 hours, forms very small white needles, melting at 61° C. (142° F.), and solidifying again at 60° C. (140° F.). — *Distearin*, $(C_3H_5)'''OH(C_{18}H_{35}O_2)_2$, obtained by heating monostearin with 3 parts of stearic acid to 260° C. (500° F.), for three hours, forms white microscopic laminæ, melts at 58° C. (136° F.), and solidifies at 55° C. (131° F.). — *Tristearin* is prepared by heating monostearin with 15 to 20 times its weight of stearic acid to 270° C. (518° F.), for three hours in a sealed tube; also from various solid natural fats by solution in ether and repeated crystallization from the hot solution. It crystallizes in masses of white pearly laminæ or needles, inodorous, tasteless, neutral, and volatilizing without decomposition under reduced pressure. Both natural and artificial tristearin exhibit three isomeric or allotropic modifications. Stearin, separated from ether, melts at 69·7° C. (157° F.); but if heated to 73·7° C. (164° F.), or higher, and then cooled, it does not solidify till cooled to 51·7° C. (124° F.). It is solid below 52° C. (125° F.), but melts at that temperature, and if heated a few degrees higher, passes into a third modification, which does not melt below 64·2° C. (148° F.).*

Arachidic Acid, $C_{20}H_{40}O_2$, is a fatty acid obtained by saponification of oil of earth-nut (*Arachis hypogæa*). It crystallizes in very small, shining scales, melts at 75° C. (167° F.), and solidifies again at 73·5° C. (164° F.), to a radiated crystalline mass. It is but slightly soluble in cold alcohol of ordinary strength, but dissolves easily in boiling absolute alcohol and in ether.

The *silver-salt*, $C_{20}H_{39}O_2Ag$, is a white precipitate, which separates from boiling alcohol in slightly lustrous prisms, not altered by exposure to light. *Ethyl arachidate*, $C_{20}H_{39}O_2 . C_2H_5$, is a crystalline mass, melting at 52·5° C. (126° F.). Berthelot has obtained three *glyceryl arachidates* or *arachins*, analogous to the stearins, by heating the acid with glycerin in sealed tubes.

Benic or **Behenic Acid**, $C_{21}H_{42}O_2$, is obtained, together with other acids, by saponification of oil of ben, the oil expressed from the fruits of *Moringa Nux Behen*. It is a white crystalline fat, melting at 76°, and solidifying at 70° C. (158° F.).

Cerotic Acid, $C_{27}H_{54}O_2$. — This acid is the essential constituent of *cerin*, the portion of bees'-wax which is soluble in boiling alcohol. It is prepared by heating the wax several times in succession with boiling alcohol, till the

* *Duffy*, Chem. Soc. Journal, vol. v., pp. 197, 303.

deposit, which forms on cooling, melts at 70° or 72° C. (158°–162° F.), and may be further purified by precipitating it from the boiling alcoholic solution with lead acetate, decomposing the precipitate with strong acetic acid, and crystallizing the separated acid from boiling alcohol. Cerotic acid is also produced by the dry distillation of Chinese wax, which consists of ceryl cerotate, $C_{27}H_{53}O_2 . C_{27}H_{55}$, or by melting that substance with potash, and decomposing the resulting potassium-salt with an acid (p. 543).

Pure cerotic acid crystallizes in small grains, melting at 78° C. (172° F.), and distilling without alteration. Chlorine converts it into chlorocerotic acid, $C_{27}H_{42}Cl_{12}O_2$, a thick transparent gum of a pale-yellow color.

Ceryl cerotate, or *Chinese wax*, is produced on certain trees in China by the puncture of a species of *coccus*. It is crystalline, of a dazzling whiteness, like spermaceti, melts at 82° C. (180° F.); dissolves in alcohol; yields cerotic acid and cerylene, $C_{27}H_{54}$, by dry distillation. It is used in China for making candles.

Melissic Acid, $C_{30}H_{60}O_2$, the highest known member of the fatty series, is obtained by heating myricyl alcohol (p. 543) with potash lime:

$$\underset{\text{Myricyl alcohol.}}{C_{30}H_{62}O_2} + KOH = \underset{\text{Potassium melissate.}}{C_{30}H_{59}O_2K} + 2H_2$$

It bears considerable resemblance to cerotic acid, but melts at a higher temperature, viz., at 88° or 89° C. (190°–192° F.). The *silver-salt*, $C_{30}H_{59}O_2Ag$, is a white precipitate.

Monatomic Acids of the Series $C_nH_{2n-2}O_2$. — Acrylic Series.

This series comprises two isomeric groups of acids: the one consisting of acids occurring in the vegetable or animal organism, or obtained from natural products by special processes; the other of acids formed by a general synthetical process: we shall designate the acids of the first group as *normal acrylic acids*, those of the second as *isoacrylic acids*.

Normal Acrylic Acids.

The following are the known acids of this group:

Acrylic acid	$C_3H_4O_2$	Physetoleic acid, Hypogæic acid, Gaïdic acid	$C_{16}H_{30}O_2$
Crotonic acid	$C_4H_6O_2$		
Angelic acid	$C_5H_8O_2$		
Pyroterebic acid	$C_6H_{10}O_2$	Oleic acid, Elaïdic acid	$C_{18}H_{34}O_2$
? Damaluric acid	$C_7H_{12}O_2$		
? Damolic acid	$C_{13}H_{24}O_2$	Doeglic acid	$C_{19}H_{36}O_2$
Moringic acid, Cimicic acid	$C_{15}H_{28}O_2$	Brassic acid, Erucic acid	$C_{22}H_{42}O_2$

Most of these acids are oily liquids. When fused with *potassium hydrate*, they yield the potassium-salt of acetic and of another acid of the fatty series, with elimination of hydrogen, thus:

$$\underset{\text{Acrylic acid.}}{C_3H_4O_2} + 2KOH = \underset{\text{Acetate.}}{C_2H_3KO_2} + \underset{\text{Formate.}}{CHKO_2} + H_2$$

$$\underset{\text{Angelic acid.}}{C_5H_8O_2} + 2KOH = \underset{\text{Acetate.}}{C_2H_3KO_2} + \underset{\text{Propionate.}}{C_3H_5KO_2} + H_2$$

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + 2KOH = \underset{\text{Acetate.}}{C_2H_3KO_2} + \underset{\text{Palmitate.}}{C_{16}H_{31}KO_2} + H_2$$

Generally:

$$C_nH_{2n-2}O_2 + 2KOH = C_2H_3KO_2 + C_{n-2}H_{2n-5}KO_2 + H_2$$

They are also converted into fatty acids by the action of nascent hydrogen; *e. g.*,

$$\underset{\text{Crotonic acid.}}{C_4H_6O_2} + H_2 = \underset{\text{Butyric acid.}}{C_4H_8O_2}$$

Acrylic Acid, $C_3H_4O_2$, is produced by the oxidation of its aldehyde, acrolein, C_3H_4O, with moist silver oxide. It is a colorless liquid, having a slightly empyreumatic odor, and miscible in all proportions with water. Its salts resemble the formates and acetates, and are for the most part very soluble in water.

Acrylic acid is converted by nascent hydrogen into propionic acid, $C_3H_6O_2$, and by bromine into dibromopropionic acid, $C_3H_4Br_2O_2$.

Crotonic Acid, $C_4H_6O_2$, is produced by saponification of the oil of *Croton Tiglium*. It is an oily liquid, having a somewhat pungent odor and an acrid taste, moderately soluble in pure water, insoluble in saline water. Heated with potassium hydrate it gives off hydrogen and forms two molecules of potassium acetate:

$$C_4H_6O_2 + 2KOH = 2C_2H_3KO_2 + H_2.$$

Angelic Acid, $C_5H_8O_2$, exists in the root of the archangel (*Angelica archangelica*), and in sumbul or moschus root, a drug imported from Asia Minor, and probably also belonging to an umbelliferous plant. It is obtained from archangel-root, by boiling the root with lime and water, and distilling the strained and concentrated liquid with dilute sulphuric acid. It is also produced by heating the essential oil of chamomile, which consists of angelic aldehyde together with a hydrocarbon, with potassium hydrate:

$$C_5H_8O + KOH = C_7H_7KO_2 + H_2.$$

Also, together with oreoselin, by treating peucedanin or imperatorin (a neutral substance contained in the root of *Imperatoria Ostruthium*, and some other umbelliferous plants), with alcoholic potash:

$$\underset{\text{Peucedanin.}}{C_{12}H_{12}O_3} + KOH = \underset{\text{Potassium angelate.}}{C_5H_7KO_2} + \underset{\text{Oreoselin.}}{C_7H_6O_2}$$

Angelic acid crystallizes in long prisms and needles, melts at 45° C. (113° F.), boils at 190° C. (374° F.), and distils without decomposition. It has an aromatic taste and odor, dissolves sparingly in cold, abundantly in hot water, also in alcohol and ether.

The angelates of the alkali-metals are soluble in water and in alcohol. *Calcium angelate*, $(C_5H_7O_2)_2Ca''$. Aq., forms shining, very soluble laminæ. The *lead-salt*, $(C_5H_7O_2)_2Pb''$, is a white precipitate.

Potassium angelate treated with phosphorus oxychloride yields angelic oxide, or anhydride, $(C_5H_7O)_2O$, which is a viscid uncrystallizable oil, boiling at 240° C. (464° F.).

Pyroterebic acid, $C_6H_{10}O_2$, is produced by dry distillation of terebic acid, $C_7H_{10}O_4$ (one of the products of the action of nitric acid on turpentine oil). It is a liquid, boiling at 210° C. (410° F.). — *Damaluric acid*, $C_7H_{12}C_2$, and *Damolic acid*, $C_{13}H_{24}O_2$, are volatile acids, said to exist in the urine of cows

and horses. — *Moringic acid*, $C_{15}H_{28}O_2$, is an oily acid obtained, together with palmitic, stearic, and benic acids, by the saponification of oil of ben (p. 625). — *Cimicic acid* is a yellow crystallizable acid, having a rancid odor, extracted by alcohol and ether from a kind of bug (*Raphigaster punctipennis*).

Hypogæic Acid, $C_{16}H_{30}O_2$, is contained, as a glyceride, together with palmitin and arachin, in oil of earth-nut (*Arachis hypogæa*). To obtain it, the mixture of fatty acids obtained by saponifying the oil, is dissolved in alcohol; the palmitic and arachidic acids are precipitated by ammonia and magnesium acetate; the filtrate is mixed with ammonia and lead acetate; the lead precipitate is decomposed by hydrochloric acid; and the separated hypogæic acid is dissolved out by ether. It is also produced by oxidation of axinic acid ($C_{18}H_{28}O_2$), an acid obtained by saponification of *age* or *axin*, a fatty substance contained in the Mexican plant *Coccus Axin.* — Hypogæic acid crystallizes from ether in stellate groups of needles, melting at 34° or 35° C. (93°–95° F.), easily soluble in alcohol and ether. Its *potassium* and *sodium salts* are soluble in water, the *barium salt* is soluble in hot, insoluble in cold water; the *copper* and *silver salts* are obtained by precipitation. The *ethylic ether*, $C_{16}H_{29}O_2 . C_2H_5$, is a yellow oil, not volatile without decomposition.

Nitrous acid converts hypogæic acid into the isomeric or allotropic compound, *Gaïdic acid*, related to it in the same manner as elaïdic acid to oleic acid. It forms a colorless crystalline mass which melts at 38° C. (100° F.).

Physetoleic acid, a crystalline acid obtained from sperm-oil, is isomeric, if not identical, with hypogæic acid; it melts at 30°, and solidifies at 28° C. (82° F.).

Oleic Acid, $C_{18}H_{34}O_2$. — This acid, the most important of the series, is obtained by saponification of olein, the fluid constituent of most natural fats and fixed oils.

To obtain pure oleic acid, olive or almond oil is saponified with potash; the soap is decomposed by tartaric acid; and the separated fatty acid, after being washed, is heated for some hours in the water-bath, with half its weight of lead oxide previously reduced to fine powder. The mixture is then well shaken up with about twice its bulk of ether, which dissolves the oleate of lead and leaves the stearate; the liquid after standing for some time is decanted and mixed with hydrochloric acid; the oleic acid thereby eliminated dissolves in the ether, and the ethereal solution, which rises to the surface of the water, is decanted, mixed with water, and freed from ether by distillation.

Large quantities of crude oleic acid are now obtained in the manufacture of stearin-candles, by treating with dilute sulphuric acid the lime-soap resulting from the action of lime upon tallow. The fatty acids resulting from the decomposition are washed with hot water, and solidify in a mass on cooling; and this mass, when subjected to pressure, yields a liquid rich in oleic acid, but still retaining a considerable quantity of stearic acid. After remaining for some time in a cold place, it deposits a quantity of solid matter, and the liquid decanted from this is sent into the market as *oleic acid* or *red oil*. It may be purified by the process just described.

Oleic acid crystallizes from alcoholic solution in dazzling white needles, melting at 14° C. (57° F.) to a colorless oil, which solidifies at 4° C. (39° F.) to a hard, white crystalline mass, expanding considerably at the same time. Specific gravity = 0·808 at 19° C. (66° F.). The acid volatilizes in a vacuum without decomposition. It is tasteless and inodorous, and reacts neutral when unaltered (not oxidized), also in alcoholic solution. It is insoluble in water, very soluble in alcohol, and dissolves in all proportions in ether. Cold strong sulphuric acid dissolves it without decomposition. It dissolves

solid fats, stearic acid, palmitic acid, &c., and is dissolved by bile, with formation of a soap and strong acid reaction.

Oleic acid, in the solid state, oxidizes but slowly in the air; but when melted, it rapidly absorbs oxygen, acquiring a rancid taste and smell and a decided acid reaction. Its decomposition by fusion with potash has been already mentioned. *Chlorine* and *bromine*, in presence of water, convert it into dichloroleic and dibromoleic acid. Bromine, added by drops to fused oleic acid, forms tribromoleic acid, $C_{18}H_{31}Br_3O_2$.

Strong *nitric acid* attacks oleic acid with violence, giving off red nitrous vapors, and producing volatile acids of the series $C_nH_{2n}O_2$, viz., acetic, propionic, butyric, valeric, caproic, œnanthylic, caprylic, pelargonic, and rutic acids; also fixed acids of the series $C_nH_{2n-4}O_2$, viz., suberic, pimelic, adipic, lipic, and azelaic acids, the number and proportion of these products varying with the duration of the action.

Nitrous acid converts oleic acid into a solid isomeric or allotropic modification, called *elaïdic acid.*

Oleates.—The formula of the neutral oleates is $C_{18}H_{33}O_2M$, or $(C_{18}H_{33}O_2)_2M''$, according to the equivalence of the metal; there are likewise acid oleates. The neutral oleates of the alkali-metals are soluble in water, and not so completely precipitated from their solutions by the addition of another soluble salt, as the stearates and palmitates. The acid oleates are liquid and insoluble in water. The oleates dissolve in cold absolute alcohol and in ether, a property by which they may be distinguished and separated from the stearates and palmitates.

Oleins. — Oleic acid forms three glycerides, viz., monolein, $(C_3H_5)'''(OH)(C_{18}H_{33}O_2)$; diolein, $(C_3H_5)'''(OH)(C_{18}H_{33}O_2)_2$; and triolein, $(C_3H_5)'''(C_{18}H_{33}O_2)_3$, which are produced by heating oleic acid and glycerin together in sealed tubes in various proportions. The first two solidify at about 15°.

The olein of animal fats, and of olive oil and several other oils, both animal and vegetable, which do not dry up in the air by slow oxidation, but are converted into viscid masses having a rancid odor and acid reaction (non-drying oils), appears to be identical with triolein, but there is great difficulty in obtaining it pure. Olive oil, cooled to 4° C. (39° F.) or a lower temperature, deposits a large quantity of solid fat, consisting mainly of palmitin (originally called *margarin*, from its pearly lustre), and the oil filtered therefrom consists mainly of olein. A purer olein is obtained by treating olive oil with a cold strong solution of caustic soda, which saponifies the solid fats, and leaves the olein unaltered. Olein, subjected to dry distillation, yields gaseous products, liquid hydrocarbons, acrolein, and sebic acid.

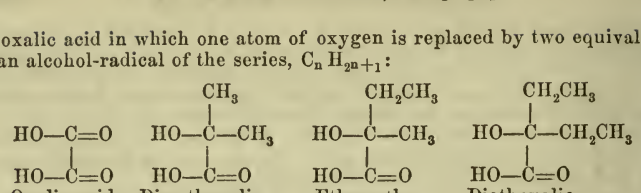
Some non-drying oils contain the glycerides of acids homologous with oleic acid; such is the case, as already observed, with croton-oil, earth-nut oil, and sperm-oil. Doegling train-oil, obtained from the doegling or bottle-nosed whale (*Balœna rostrata*), yields *doeglic acid*, $C_{19}H_{36}O_2$. Colza-oil, obtained from the seeds of certain species of *Brassica*, especially the summer rape or colza, *Brassica campestris*, var. *oleifera*, yields *brassic acid*, $C_{22}H_{42}O_2$; and the oil of black mustard-seed yields a similar and probably identical acid, called *erucic acid.*

Drying oils, such as linseed and poppy oils, and castor-oil which is a non-drying oil, contain the glycerides of acids belonging to other series, which will be noticed hereafter.

Iso-acrylic Acids.

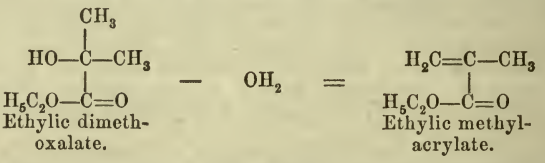
Acids isomeric with the natural acrylic acids are produced by abstraction of the elements of water from certain acid ethers, having the composition

of oxalic acid in which one atom of oxygen is replaced by two equivalents of an alcohol-radical of the series, C_nH_{2n+1}:



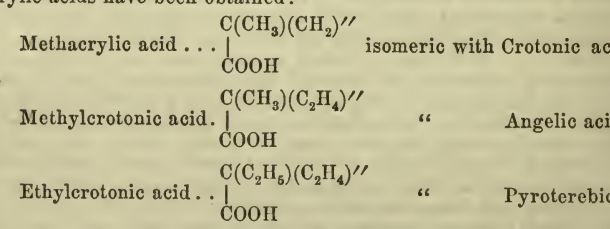
Oxalic acid. Dimethoxalic acid. Ethomethoxalic acid. Diethoxalic acid.

Now, when the ethylic ethers of these acids are treated with phosphoric oxide or phosphorus trichloride, they give up a molecule of water (OH_2), at the expense of one of the molecules of hydroxyl (OH) and an atom of hydrogen abstracted from one of the monad alcohol-radicals, which is thereby converted into a dyad radical (an olefine) capable of saturating the unit of equivalence of the carbon-atom set free by abstraction of the hydroxyl. The product is the ethylic ether of an iso-acrylic acid; thus,



Ethylic dimethoxalate. Ethylic methylacrylate.

The ethylic ether thus formed is converted into methacrylic acid by saponification with potash in the usual way. In this manner the following isoacrylic acids have been obtained:

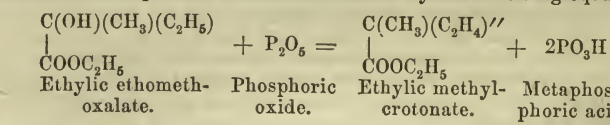


Methacrylic acid . . . isomeric with Crotonic acid

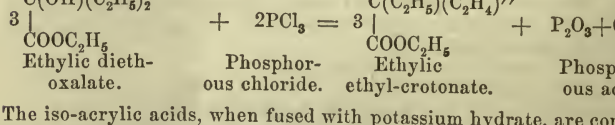
Methylcrotonic acid. " Angelic acid

Ethylcrotonic acid . . " Pyroterebic acid

The actual formation of the ethers of these acids, by the action of phosphoric oxide and phosphorous chloride on the oxalic compounds above mentioned, takes place in the manner shown by the following equations:



Ethylic ethomethoxalate. Phosphoric oxide. Ethylic methylcrotonate. Metaphosphoric acid.



Ethylic diethoxalate. Phosphorous chloride. Ethylic ethyl-crotonate. Phosphorous acid.

The iso-acrylic acids, when fused with potassium hydrate, are converted, like the normal acrylic acids, into two acids of the acetic series. The dyad radical of the iso-acrylic acid is displaced by two atoms of hydrogen derived from two molecules of potassium hydrate (2KOH), and enters into

combination with two atoms of oxygen; and at the same time the two atoms of potassium displace the basic hydrogen-atoms of the two acids thus produced, converting them into potassium-salts, and expelling the hydrogen as gas; thus:

$$\underset{\text{Methacrylic acid.}}{C(CH_2)''CH_3 \\ | \\ COOH} + 2KOH = \underset{\text{Propionate.}}{CH_2CH_3 \\ | \\ COOK} + \underset{\text{Formate.}}{H \\ | \\ COOK} + H_2$$

$$\underset{\text{Methyl-crotonic acid.}}{C(C_2H_4)''CH_3 \\ | \\ COOH} + 2KOH = \underset{\text{Propionate.}}{CH_2CH_3 \\ | \\ COOK} + \underset{\text{Acetate.}}{CH_3 \\ | \\ COOK} + H_2$$

$$\underset{\text{Ethyl-crotonic acid.}}{C(C_2H_4)''C_2H_5 \\ | \\ COOH} + 2KOH = \underset{\text{Butyrate.}}{CH_2C_2H_5 \\ | \\ COOK} + \underset{\text{Acetate.}}{CH_3 \\ | \\ COOK} + H_2$$

The normal acrylic acids are decomposed by potash in a similar manner, yielding two acids of the series, $C_nH_{2n}O_2$; but one of these is always acetic acid. Hence it is inferred that they have a constitution represented by the formula $\begin{matrix} C(C_nH_{2n})''H \\ | \\ COOH \end{matrix}$, and that their decomposition by potash is represented by the equation:

$$\underset{\text{Iso-acrylic acid.}}{C(C_nH_{2n})''H \\ | \\ COOH} + 2OH_2 = \underset{\text{Acetic acid.}}{CH_3 \\ | \\ COOH} + \underset{\text{Homologue of acetic acid.}}{C_{n-1}H_{2n-1} \\ | \\ COOH} + H_2$$

The formulæ of the individual acids are as follows:

$CH(CH_2)''$	$CH(C_2H_4)''$	$CH(C_3H_6)''$	$CH(C_4H_8)''$	$\cdots$	$CH(C_{16}H_{32})$
COOH	COOH	COOH	COOH		COOH
Acrylic.	Crotonic.	Angelic.	Pyroterebic.		Oleic.

It is easily seen from these formulæ that crotonic acid, when decomposed by an alkali, must yield two molecules of acetic acid; and that the other acids above formulated must yield acetic acid together with formic, propionic, butyric, and palmitic acids respectively.

An acid isomeric with crotonic acid, and differing from methacrylic acid, has been obtained by boiling allyl cyanide with caustic potash:

$$C_3H_5CN + KOH + OH_2 = NH_3 + C_4H_5KO_2$$

Frankland assigns to this acid the composition $\begin{matrix} CH(CH_2)'' \\ | \\ CH_2 \\ | \\ COOH \end{matrix}$

There is also an acid called *campholic acid*, $C_{10}H_{16}O_2$, produced by heating common camphor, $C_{10}H_{16}O$, with potassium hydrate. It cannot be included in either of the series of acrylic acids, inasmuch as it does not exhibit the

reactions of either. It is a white crystalline body, insoluble in water, soluble in alcohol and ether, decomposed by distillation with phosphoric oxide, into carbon monoxide, water, and campholene, C_9H_{16}.

Monatomic Acids belonging to the series $C_nH_{2n-4}O_2$, or $C_nH_{2n-5}O(OH)$.

Only three acids of this series are known, viz.: sorbic and parasorbic acids, both having the composition $C_6H_8O_2$, and camphic acid, $C_{10}H_{16}O_2$.

Parasorbic acid is a volatile oily acid obtained from mountain-ash berries; *sorbic acid* is a crystallizable acid produced from it by gentle heating with solid potash, or boiling with strong hydrochloric acid; it melts at 134·5° C. (274° F.), volatilizes without decomposition, and decomposes carbonates.

Camphic acid, $C_{10}H_{16}O_2$, is obtained, together with the corresponding alcohol, camphol (p. 546), by heating common camphor with alcoholic soda-solution in sealed tubes to 170°–190° C. (338°–374° F.).

$$\underset{\text{Camphor.}}{2C_{10}H_{16}O} + OH_2 = \underset{\text{Camphol.}}{C_{10}H_{18}O} + \underset{\text{Camphic acid.}}{C_{10}H_{16}O_2}$$

By neutralizing the resulting alkaline solution with sulphuric acid, dissolving out the sodium camphate with alcohol, evaporating, and again adding sulphuric acid, the camphic acid is obtained as a solid mass heavier than water, insoluble therein, easily soluble in alcohol. The potassium and sodium salts are insoluble in strong alkaline lyes. They precipitate the salts of copper, iron, silver, and zinc, not those of the alkali-metals; all the precipitates are soluble in a large quantity of water.

Monatomic Acid belonging to the series $C_nH_{2n-6}O_2$.

Hydrobenzoic acid, $C_7H_{10}O_2$, or $C_7H_9O(OH)$.*—This acid, corresponding to the unknown alcohol, $C_7H_{12}O$, is formed, together with other products, by the action of sodium amalgam on benzoic acid:

$$\underset{\text{Benzoic acid.}}{C_7H_6O_2} + 2H_2 = \underset{\text{Hydrobenzoic acid.}}{C_7H_{10}O_2}$$

It is more easily obtained, however, by boiling hydrobenzyluric acid (a product of the decomposition of hippuric acid by sodium amalgam) with alkalies in a close vessel:

$$\underset{\text{Hydrobenzyluric acid.}}{C_{16}H_{21}NO_4} + OH_2 = \underset{\text{Glycocine.}}{C_2H_5NO_2} + \underset{\text{Benzyl alcohol.}}{C_7H_8O} + \underset{\text{Hydrobenzoic acid.}}{C_7H_{10}O_2}$$

It is a crystalline acid, forming a crystalline calcium salt, $(C_7H_9O_2)_2Ca$, and, when recrystallized either in the free state or in the form of calcium salt, is ultimately converted by oxidation into benzoic acid. Its ethylic ether, $C_7H_9O_2.C_2H_5$, has the odor of ethyl valerate.

* *M. Hermann*, Ann. Ch. Pharm. cxxxii. 75. — *R. Otto, ibid.* cxxxiv. 303.

Monatomic Acids belonging to the series $C_nH_{2n-8}O_2$. — Aromatic Acids.

These acids are produced by some of the processes which yield the fatty acids, viz.—1. By the oxidation of the corresponding aldehydes and primary alcohols: thus benzoic acid, $C_7H_8O_2$, is formed by oxidation of benzoic aldehyde, C_7H_6O, and of benzylic alcohol, C_7H_8O. — 2. By the action of water on the corresponding acid chlorides. — 3. By the action of alkalies on the cyanides of aromatic alcohol-radicals.

They are likewise obtained: 4. By the simultaneous action of sodium and carbon dioxide on the monobrominated derivatives of the aromatic hydrocarbons: thus,

$$\underset{\text{Bromo-benzene.}}{C_6H_5Br} + Na + CO_2 = NaBr + \underset{\text{Sodium benzoate.}}{C_7H_5NaO_2}$$

5. Certain aromatic acids are produced by the oxidation of hydrocarbons homologous with benzene.

The known acids of this series are:

Benzoic acid, $C_7H_6O_2$.
Toluic and Alpha-toluic acids, $C_8H_8O_2$.
Xylic and Alpha-xylic acids, $C_9H_{10}O_2$.
Cumic acid, $C_{10}H_{12}O_2$, homologous with toluic acid.
Alpha-cymic acid, $C_{11}H_{14}O_2$, homologous with alpha-toluic acid.

Benzoic Acid, $C_7H_6O_2 = C_7H_5O(OH)$.—This acid is the analogue of benzylic alcohol, and is produced from it by oxidation with aqueous chromic acid:

$$\underset{\text{Benzyl alcohol.}}{C_6H_5.CH_2OH} + O_2 = OH_2 + \underset{\text{Benzoic acid.}}{C_6H_5.COOH}$$

It is also formed by oxidation of benzoic aldehyde, C_7H_6O (bitter-almond oil), in presence of platinum black, or with nitric acid.

It may be produced directly from benzene, by acting upon that compound in the state of vapor with carbonyl chloride (phosgene gas) whereby it is converted into benzoyl chloride, and decomposing this chloride with water:

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Carbonyl chloride.}}{COCl_2} = HCl + \underset{\text{Benzoyl chloride.}}{C_7H_5OCl}$$

$$\underset{\text{Benzoyl chloride.}}{C_7H_5OCl} + OH_2 = HCl + \underset{\text{Benzoic acid.}}{C_7H_5O(OH)}$$

Fourthly, it is obtained by boiling hippuric acid (or the urine of cows or horses which contains that acid) with hydrochloric acid. The hippuric acid, $C_9H_9NO_3$, which has the composition of benzoyl-glycocine, then takes up a molecule of water, and is resolved into glycocine (p. 614) and benzoic acid:

$$\underset{\text{Hippuric acid.}}{C_2H_4(C_7H_5O)NO_2} + OH_2 = \underset{\text{Glycocine.}}{C_2H_5NO_2} + \underset{\text{Benzoic acid.}}{C_7H_6O_2}$$

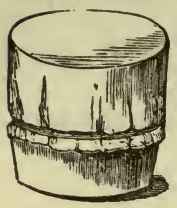
This process is applied to the preparation of benzoic acid on the large scale.

Benzoic acid is also produced by the oxidation of a great variety of or-

ganic bodies, as cumene, cinnamic aldehyde, cinnamic acid, cinnamene, casein, gelatin, &c.

Benzoic acid exists ready formed in large quantity in several balsams and gum-resins, especially in gum-benzoin, a resin which exudes from the bark of *Styrax benzoin*, a tree growing in Sumatra, Java, Borneo, and Siam. When this substance is exposed to a gentle heat in a subliming vessel, the benzoic acid is volatilized, and may be condensed. The simplest and most efficient apparatus for this and all similar operations is the contrivance of Dr. Mohr: it consists of a shallow iron pan, over the bottom of which the substance to be sublimed is thinly spread; a sheet of bibulous paper, pierced with a number of pin-holes, is then stretched over the vessel, and a cap made of thick, strong drawing or cartridge-paper, is secured by a string or hoop over the whole. The pan is placed upon a sand-bath, and slowly heated to the requisite temperature; the vapor of the acid condenses in the cap, and the crystals are kept by the thin paper diaphragm from falling back again into the pan. Benzoic acid thus obtained assumes the form of light, feathery, colorless crystals, which exhale a fragrant odor, not belonging to the acid itself, but due to a small quantity of volatile oil. A more productive method of preparing the acid is to mix the powdered gum-benzoin very intimately with an equal weight of slaked lime, boil this mixture with water, and decompose the filtered solution, concentrated by evaporation to a small bulk, with excess of hydrochloric acid; the benzoic acid crystallizes out on cooling in thin plates, which may be drained upon a cloth filter, pressed, and dried in the air. By sublimation, which is then effected with trifling loss, the acid is obtained perfectly white.

Fig. 194.



Benzoic acid is inodorous when cold, but acquires a faint smell when gently warmed: it melts just below 121° C. (250° F.), and sublimes at a temperature a little above; it boils at 249° C. (480° F.), and emits a vapor of the density of 4·27. It dissolves in about 200 parts of cold and 25 parts of boiling water, and with great facility in alcohol. Benzoic acid is not affected by ordinary nitric acid, even at boiling heat; but with *fuming nitric acid* it forms a substitution-product.—*Chlorine* also acts on benzoic acid, forming substitution-products.—*Phosphorus pentachloride* converts it into benzoyl chloride, C_7H_5OCl.—Benzoic acid dissolves in ordinary strong sulphuric acid, but is precipitated unaltered on addition of water. By fuming sulphuric acid, however, and still more readily by sulphuric oxide, it is converted into sulphobenzoic acid, $C_7H_6SO_5$, a bibasic acid to be described hereafter. By nascent hydrogen (evolved by sodium-amalgam) it is partly reduced to benzoic aldehyde and benzylic alcohol, and is partly converted, by addition of hydrogen, into hydrobenzoic acid, $C_7H_{10}O_2$ (p. 632).

All the *benzoates* are more or less soluble: they are easily formed, either directly or by double decomposition. The *benzoates of the alkalies* and of *ammonia* are very soluble, and somewhat difficult to crystallize. — *Calcium benzoate* forms groups of small colorless needles, which require 20 parts of cold water for solution. The *barium salts* are soluble with difficulty in the cold. Neutral *ferric benzoate* is a soluble compound; but the basic salt obtained by neutralizing as nearly as possible with ammonia a solution of ferric oxide, and then adding ammonium benzoate, is quite insoluble. Iron is sometimes thus separated from other metals in quantitative analysis. Neutral and basic *lead benzoate* are freely soluble in the cold. *Silver benzoate* crystallizes in thin transparent plates, which blacken on exposure to light.

Calcium benzoate is resolved by dry distillation into calcium carbonate and benzone, or benzophenone, $C_{13}H_{10}O$, the ketone of benzoic acid:

$$\underset{\text{Calcium benzoate.}}{(C_7H_5O_2)_2Ca''} = CO_3Ca + \underset{\text{Benzone.}}{CO(C_6H_5)_2}$$

On the other hand, benzoic acid, distilled with excess of lime, is resolved into carbon dioxide and benzene:

$$C_7H_6O_2 = CO_2 + C_6H_6.$$

Benzoic Chloride, or Benzoyl Chloride, C_7H_5OCl. — This compound, derived from benzoic acid by substitution of chlorine for hydroxyl, is prepared by the action of phosphorus pentachloride on benzoic acid:

$$C_7H_5O(OH) + PCl_3Cl_2 = POCl_3 + HCl + C_7H_5OCl.$$

The two substances are mixed in equivalent quantities, and gently heated. A brisk reaction ensues, hydrochloric acid is evolved, while oxychloride of phosphorus distils over; and when the temperature rises to 196° C. (384° F.), the receiver is to be changed, and the benzoyl chloride, which passes over at that temperature, collected separately. It may also be prepared by subjecting bitter-almond oil (C_7H_6O) to the action of dry chlorine gas. It is a colorless liquid of peculiar, disagreeable, and pungent odor; its density is 1·106. The vapor is inflammable, and burns with a greenish flame; its density (referred to air) is 4·987. Benzoyl chloride is decomposed slowly by cold and quickly by boiling water into benzoic and hydrochloric acids: with an alkaline hydrate, a benzoate, and chloride of the alkalic metal, are generated.

Benzoyl Iodide, C_7H_5OI, is prepared by distilling the chloride with potassium iodide: it forms a colorless, crystalline, fusible mass, decomposed by water and alkalies in the same manner as the chloride. The *bromide*, C_7H_5OBr, has very similar properties. *Benzoyl cyanide*, $C_7H_5O.CN$, obtained by heating the chloride with mercuric cyanide, forms a crystalline mass, fusing at 31° C. (87° F.), boiling at 207° C. (404° F.), and having a pungent odor, somewhat resembling that of cinnamon. All these compounds yield benzamide with dry ammonia.

Benzoyl Oxide, or Anhydride, $C_{14}H_{10}O_3$, or $(C_7H_5O)_2O$, is obtained by the action of benzoyl chloride on potassium benzoate:

$$C_7H_5O(ONa) + C_7H_5OCl = NaCl + (C_7H_5O)_2O.$$

Benzoyl chloride acts in like manner on acetate or valerate of sodium, forming aceto-benzoic or valero-benzoic oxide, either of which splits up on distillation into acetic or valeric oxide and benzoic oxide:

$$\underset{\text{Benzyl chloride.}}{C_7H_5OCl} + \underset{\text{Sodium valerate.}}{C_5H_9O(ONa)} = NaCl + \underset{\text{Valero-benzoic oxide.}}{\left.\begin{matrix}C_7H_5O\\C_5H_9O\end{matrix}\right\}O}$$

and:

$$\underset{\text{Valero-benzoic oxide.}}{2\left\{\begin{matrix}C_7H_5O\\C_5H_9O\end{matrix}\right\}O} = \underset{\text{Benzoic oxide.}}{(C_7H_5O)_2O} + \underset{\text{Valeric oxide.}}{(C_5H_9O)_2O}$$

Benzo-œnanthylic, benzostearic, benzo-angelic, benzo-cuminic oxide, and several others, have been obtained by similar processes.

Benzoic oxide crystallizes in oblique rhombic prisms, melting at 42° C.

(107° F.), and distilling undecomposed at 310° C. (590° F.). It melts in boiling water, remaining fluid for a long time, but is ultimately converted into benzoic acid, and dissolves: caustic alkalies effect the conversion much more rapidly. With ammonia it forms ammonium benzoate and benzamide:

$$\underset{\text{Benzoic oxide.}}{(C_7H_5O)_2O} + 2NH_3 = \underset{\text{Ammonium benzoate.}}{C_7H_5O(NH_4)O} + \underset{\text{Benzamide.}}{NH_2C_7H_5O}$$

Benzoyl Dioxide, or Peroxide, $C_{14}H_{10}O_4$, or $(C_7H_5O_2)_2$. — Brodie obtained this compound by bringing benzoyl chloride in contact with barium dioxide under water; the product, when re-crystallized from ether, yields large shining crystals of benzoyl dioxide, which explode when heated. When submitted to the action of a boiling solution of potash, this substance evolves oxygen, and forms potassium benzoate.

Benzoyl Sulphide, $(C_7H_5O)_2S$, obtained by distilling the chloride with finely powdered lead sulphide, is a yellow fetid oil, solidifying at a low temperature to a soft crystalline mass.

Dibenzoyl, $C_{14}H_{10}O_4$. — Cupric benzoate subjected to gradual dry distillation, gives a residue containing salicylic and benzoic acids, and an oily distillate which crystallizes on cooling, and consists of dibenzoyl. This substance possesses the odor of the geranium, melts at 70° C. (158° F.). It was discovered by Ettling, and subsequently studied by Stenhouse. By heating with potassium hydrate, it is instantly converted into benzoic acid, with evolution of hydrogen.

Acids derived from Benzoic Acid by substitution.

Chlorobenzoic Acid, $C_7H_5ClO_2$, is obtained by treating benzoic acid with potassium chlorate and hydrochloric acid. Acids having the same composition are produced by the action of chlorine upon benzoic acid in sunlight, and also by distilling sulphobenzoic acid, salicylic acid, or hippuric acid, with phosphorus pentachloride, and boiling the distillate with water. The acids obtained by these several methods, however, differ in their properties. Chlorobenzoic acid treated with sodium amalgam and water is converted into benzoic acid.

Bromobenzoic Acid, $C_7H_5BrO_2$, is formed by the action of bromine on silver benzoate:

$$C_7H_5O_2Ag + Br_2 = AgBr + C_7H_5BrO_2.$$

Bromine does not act on benzoic acid at ordinary temperatures.

Nitrobenzoic Acid, $C_7H_5(NO_2)O_2$, is obtained by boiling benzoic acid for several hours with fuming nitric acid; and by prolonged action of the fuming nitric acid, or more readily by the action of a mixture of nitric and sulphuric acids, *dinitrobenzoic acid*, $C_7H_4(NO_2)_2O_2$, is produced. Both these are crystalline bodies, analogous in most of their reactions to benzoic acid.

Amidobenzoic Acids. — Nitrobenzoic and dinitrobenzoic acids are reduced, by treatment with certain reducing agents, as hydrogen sulphide or ammonium sulphide, to *amido-benzoic* and *diamido-benzoic acids:*

$$\underset{\text{Nitrobenzoic acid.}}{C_7H_5(NO_2)O_2} + 3SH_2 = 2OH_2 + S_3 + \underset{\text{Amidobenzoic acid.}}{C_7H_5(NH_2)O_2}$$

$$\underset{\text{Dinitrobenzoic acid.}}{C_7H_4(NO_2)_2O_2} + 6SH_2 = 4OH_2 + S_6 + \underset{\text{Diamido-benzoic acid.}}{C_7H_4(NH_2)_2O_2}$$

Both these are crystalline compounds. Amidobenzoic acid is a monobasic acid, forming metallic salts and ethers; diamidobenzoic acid, on the contrary, possesses no acid properties, but is rather a base, combining readily with hydrochloric and other acids, and forming crystallizable salts.

When amidobenzoic acid, $C_7H_7NO_2$, is subjected to the action of nitrous acid, two molecules of it give up three atoms of hydrogen in exchange for one atom of nitrogen, and are converted into a compound containing $C_{14}H_{11}N_3O_4$.

$$2C_7H_7NO_2 + NO_2H = 2OH_2 + C_{14}H_{11}N_3O_4.$$

This substitution of hydrogen for nitrogen was first observed by Griess, who has since shown that it is susceptible of very general application.

By the prolonged action of nitrous acid, the compound $C_{14}H_{11}N_3O_4$ is partially converted into oxybenzoic acid, $C_7H_6O_2$.

ACETAMIDOBENZOIC ACID,* $C_9H_9NO_3 = C_7H_5[NH(C_2H_3O)]O_2$, or $C_7H_4\begin{matrix}NH(CH_3O)\\ |\\ COOH\end{matrix}$. — This acid is produced by digesting amidobenzoic acid with acetic acid at 130°–140° C. (266°–284° F.) in a sealed tube:

$$\underset{\text{Amidobenzoic acid.}}{C_7H_5(NH_2)O_2} + \underset{\text{Acetic acid.}}{C_2H_3O(OH)} = OH_2 + \underset{\text{Acetamidobenzoic acid.}}{C_7H_5[NH(C_2H_3O)]O_2},$$

or by the action of acetyl chloride or acetic acid on zinc amidobenzoate:

$$\underset{\text{Zinc oxybenzoate.}}{(C_7H_6NO_2)_2Zn''} + \underset{\text{Acetyl chloride.}}{2C_2H_3OCl} = ZnCl_2 + \underset{\text{Acetamidobenzoic acid.}}{2C_7H_6(C_2H_3O)NO_2}$$

Acetamidobenzoic acid is a white powder, consisting of microscopic crystals, insoluble in cold water and ether, slightly soluble in boiling water, easily in boiling alcohol. It is a monobasic acid, forming easily soluble salts with the metals of the alkalies and alkaline earths; sparingly soluble salts with lead, silver, and zinc. By boiling with hydrochloric or dilute sulphuric acid, it is resolved into acetic and amidobenzoic acids:

$$C_9H_9NO_3 + OH_2 = C_2H_4O_2 + C_7H_7NO_2.$$

HIPPURIC ACID, OR BENZAMIDACETIC ACID, $C_9H_9NO_3 = C_2H_4(C_7H_5O)NO_2 = C_2H_3[NH(C_7H_5O)]O_2$ or $\begin{matrix}C_2H_2NH(C_6H_5O)\\ |\\ COOH\end{matrix}$. — This acid, isomeric with acetamidobenzoic acid, is produced by the action of benzoyl chloride on the zinc salt of amidacetic acid (glycocine):

$$(C_2H_4NO_2)_2Zn'' + 2C_7H_5OCl = ZnCl_2 + 2C_2H_3[NH(C_7H_5O)]O_2;$$

the reaction being analogous to the second of those above given for the formation of acetamidobenzoic acid.

Hippuric acid occurs, often in large quantity, as a potassium or sodium-salt, in the urine of horses, cows, and other graminivorous animals; in smaller quantity also in human urine. It is prepared by evaporating in a water-bath perfectly fresh cows' urine to about a tenth of its volume, filtering from the deposit, and then mixing the liquid with excess of hydrochloric acid. Cows' urine frequently deposits hippuric acid without concentration, when mixed with a considerable quantity of hydrochloric acid, in which the acid is less soluble than in water. The brown crystalline

* *G. C. Foster*, Chem. Soc. Journal, xiii. 235.

mass, which separates on cooling, is dissolved in boiling water, and treated with a stream of chlorine gas, until the liquid assumes a light amber color, and begins to smell of chlorine: it is then filtered and left to cool. The still impure acid is re-dissolved in water, neutralized with sodium carbonate, and boiled for a short time with animal charcoal: the hot filtered solution is, lastly, decomposed by hydrochloric acid.

Hippuric acid crystallizes in long, slender, milk-white, and exceedingly delicate square prisms, which have a slightly bitter taste, melt on the application of heat, and require for solution about 400 parts of cold water: it also dissolves in hot alcohol. It has an acid reaction, and forms salts with bases, many of which are crystallizable. Exposed to a high temperature, hippuric acid undergoes decomposition, yielding benzoic acid, ammonium benzoate, and benzonitrile, with a coaly residue. With hot oil of vitriol, it gives off benzoic acid; boiling hydrochloric acid converts it into benzoic acid and amidacetic acid or glycocine:

$$\underset{\text{Hippuric acid.}}{C_2H_4(C_7H_5O)NO_2} + \underset{\text{Water.}}{H(OH)} = \underset{\text{Benzoic acid.}}{C_7H_5O(OH)} + \underset{\text{Amidacetic acid.}}{C_2H_5NO_2},$$

just as acetamidobenzoic acid is resolved into acetic and amidobenzoic acids.

Hippuric acid, treated with nitrous acid, gives off nitrogen, and is converted into *benzoglycollic acid*, an acid containing the elements of benzoic and glycollic (oxyacetic) acids, minus one molecule of water:

$$\underset{\text{Hippuric acid.}}{C_9H_9NO_3} + \underset{\text{Nitrous acid.}}{NO_2H} = \underset{\text{Benzoglycollic acid.}}{C_9H_8O_4} + OH_2 + N_2$$

Benzoglycollic acid, when boiled with water, splits up into benzoic and glycollic acids:

$$C_9H_8O_4 + OH_2 = C_7H_6O_2 + C_2H_4O_3.$$

If, in the preparation of hippuric acid, the urine be in the slightest degree putrid, the hippuric acid is all destroyed during the evaporation, ammonia is disengaged in large quantity, and the liquid is then found to yield nothing but benzoic acid, not a trace of which can be discovered in the unaltered secretion. Complete putrefaction effects the same change: benzoic acid might thus be procured to almost any extent. When benzoic acid is taken internally, it is rejected from the system in the state of hippuric acid, which is then found in the urine.

Hippuric acid is monobasic, the formula of the hippurates of monatomic metals being $C_9H_8MNO_3$. Most metallic oxides dissolve readily in hippuric acid. The hippurates of potassium, sodium, and ammonium, are very soluble, and difficult to crystallize; their solutions form a cream-colored precipitate with ferric salts, and white curdy precipitates with silver nitrate and mercurous nitrate. A characteristic reaction of the hippurates is, that, when fused with excess of potash or lime, they give off ammonia and yield benzene by distillation. Mineral acids decompose them, separating the hippuric acid.

Hippuric acid dissolves so abundantly in an aqueous solution of sodium phosphate, that this solution loses its alkaline reaction and becomes acid. This reaction may explain the acid character of the recent urine of man and animals.

Toluic Acid, $C_8H_8O_2 = C_8H_7O(OH)$.—This formula includes two isomeric acids, viz.:

Normal toluic acid, $C_6H_4(CH_3).COOH$, corresponding to xylylic alcohol, $C_6H_4(CH_3).CH_2OH$, derived from dimethyl-benzene (p. 497).

Alpha-toluic acid, $O_6H_5 . CH_2COOH$, corresponding to the unknown alcohol, $C_6H_5 . CH_2CH_2OH$, derived from ethyl-benzene.

Normal toluic acid is produced — 1. By oxidation of xylene with dilute nitric acid:

$$C_8H_{10} + O_3 = OH_2 + C_8H_8O_2$$

Also by the prolonged action of dilute nitric acid on cymene (p. 500), oxalic acid being formed at the same time:

$C_{10}H_{14}$	+	O_8	=	$C_8H_8O_2$	+	$C_2H_2O_4$	+	$2OH_2$
Cymene.				Toluic acid.		Oxalic acid.		

2. Synthetically, by the action of sodium and carbon dioxide on bromo-toluene:

C_7H_7Br	+	Na_2	+	CO_2	=	NaBr	+	$C_7H_7 . CO_2Na$
Bromo-toluene.								Sodium toluate.

Toluic acid is precipitated by acids from the solution of its salts as a white crystalline mass, which melts at about 175° C. (347° F.), and sublimes without decomposition in fine needles. Its chemical reactions are analogous to those of benzoic acid. By distillation with lime or baryta it is resolved into carbon dioxide and toluene, C_7H_8. Distilled with phosphorus pentachloride, it yields *toluic chloride*, C_8H_7OCl, or $C_6H_4CH_3 . COCl$. Strong nitric acid, at the boiling heat, converts it into *nitrotoluic acid*, $C_8H_7(NO_2)O_2$. When introduced into the animal organism, it is excreted as *toluric acid*, $C_{10}H_{11}NO_3$, a homologue of hippuric acid.

Alpha-toluic acid, $C_6H_5 . CH_2CO_2H$, is produced by boiling benzyl cyanide with strong potash solution as long as ammonia is given off:

$C_6H_5 . CH_2CN$	+	$2OH_2$	=	NH_3	+	C_6H_5 CH_2COOH
Benzyl-cyanide.						Alpha-toluic acid.

The reaction amounts to an interchange between an atom of trivalent nitrogen and the group O″(OH): hence the constitution of the acid is apparent.

Alpha-toluic acid crystallizes from boiling water in broad, thin laminæ, very much like benzoic acid: it has an odor like that of the perspiration of horses. It melts at 76·5° C. (169° F.), gives off, even below 100°, vapors which excite coughing, and boils at 265·5° C. (510° F.). It forms a substitution-product with nitric acid, and when distilled with phosphorus pentachloride, yields *alpha-toluic chloride*, C_8H_7OCl, or $C_6H_5 . CH_2COCl$, which passes over as a colorless heavy liquid.

Xylic Acid, $C_9H_{10}O_2 = C_6H_3(CH_3)_2 . CO_2H$, homologous with benzoic and with normal toluic acid, is produced by the action of sodium and carbon dioxide on bromo-xylene, C_8H_9Br; also, by oxidizing cumene, C_9H_{12}, with nitric acid. Insolinic acid, $C_9H_8O_4$, is formed at the same time, but the two acids are easily separated by distillation, the xylic acid passing over, while the insolinic acid remains behind. Xylic acid crystallizes from boiling water in needles, melts at 103° C. (217° F.), boils at 273° C. (523° F.), and sublimes easily in needles.

Alpha-xylic acid, $C_6H_4(CH_3) . CH_2CO_2H$, is obtained by boiling xylyl chloride with potassium cyanide (whereby xylyl cyanide, C_8H_9Cl, is produced), and then with potash. It crystallizes in broad needles, having a satiny lustre, easily soluble in water, and boiling at 42° C. (108° F.).

Cumic Acid, $C_{10}H_{12}O_2$, probably $C_6H_4(C_3H_7) . CO_2H$, homologous with ben-

zoic and normal toluic acids, is produced by oxidation of cuminol or cumic aldehyde, $C_{10}H_{12}O$, one of the constituents of oil of cumin. It is very much like benzoic acid, is converted by fuming nitric acid into nitrocumic acid, $C_{10}H_{11}(NO)_2O_4$, and resolved, by distillation with lime, into carbon dioxide and cumene, C_9H_{12}.

Cymic Acid, $C_{11}H_{14}O_2$. — Normal cymic acid is not known, but alphacymic acid, probably $C_6H_3(C_2H_5)_2COOH$, is produced by the action of caustic alkalies on cymyl cyanide, $C_{10}H_{13}CN$.

Monatomic Acids, $C_nH_{2n-10}O_2$.

The acids of this series are related to the aromatic acids, in the same manner as those of the acrylic series to the fatty acids. Only two of them, however, are at present known, viz.: cinnamic and atropic acids, both containing $C_9H_8O_2$.

CINNAMIC ACID, $C_9H_8O_2 = C_9H_7O(OH) = \begin{matrix} CH(C_7H_6)'' \\ | \\ CO_2H \end{matrix}$. — This acid is produced synthetically: 1. By heating benzoic aldehyde in close vessels with acetyl chloride:

$$C_7H_6O + C_2H_3OCl = HCl + C_9H_8O_2.$$

2. By treating potassium benzoate with chlorethylidene (produced by the action of carbonyl chloride on acetic aldehyde):

C_2H_4O	+	$COCl_2$	=	HCl	+	CO_2	+	C_2H_3Cl
Aldehyde.		Carbonyl chloride.						Chlorethylidene.

C_2H_3Cl	+	$C_7H_5O_2K$	=	KCl	+	$C_9H_8O_2$
Chlorethylidene.		Potassium benzoate.				Cinnamic acid.

Cinnamic acid is also produced by oxidation of cinnamon-oil (cinnamic aldehyde, C_9H_8O) in air or oxygen, and exists ready formed, together with benzoic acid, and certain oily and resinous substances, in Peru and Tolu balsams, being doubtless produced by oxidation of cinnyl alcohol or styrone, $C_9H_{10}O$ (p. 554), likewise contained therein. It may be procured by the following process in great abundance, and in a state of perfect purity. Old, hard Tolu balsam is reduced to powder and intimately mixed with an equal weight of slaked lime: this mixture is boiled for some time in a large quantity of water, and filtered hot. On cooling, calcium cinnamate crystallizes out, while calcium benzoate remains in solution. The impure salt is redissolved in boiling water, digested with animal charcoal, and, after filtration, suffered to crystallize. The crystals are drained and pressed, once more dissolved in hot water, and an excess of hydrochloric acid being added, the whole is allowed to cool. The pure cinnamic acid separates in small plates or needle-formed crystals of perfect whiteness. From the original mother-liquor much benzoic acid may be procured.

The crystals of cinnamic acid are smaller and less distinct than those of benzoic acid, which in most respects it very closely resembles. It melts at 120° C. (248° F.), and enters into ebullition at 293° C. (560° F.); the vapor is pungent and irritating. Cinnamic acid is much less soluble, both in hot and cold water, than benzoic acid; a hot saturated solution becomes on

cooling a soft solid mass of small nacreous crystals. It dissolves with perfect ease in alcohol. Boiling nitric acid decomposes cinnamic acid with great energy, and with production of copious red fumes: bitter almond-oil distils over, and benzoic acid remains in the retort. When cinnamic acid is heated in a retort with a mixture of strong solution of potassium bichromate and sulphuric acid, it is almost instantly converted into benzoic acid, which afterwards distils over with the vapor of water; the odor of bitter-almond oil is at the same time very perceptible. Cinnamic acid fused with excess of potassium hydrate, is decomposed into benzoic and acetic acids:

$$C_9H_8O_2 + 2OH_2 = C_7H_6O_2 + C_2H_4O_2 + H_2.$$

This decomposition is precisely analogous to that of an acid of the acrylic series into two acids of the fatty series (p. 626).

Cinnamic acid is resolved by distillation with lime or baryta, and partially also, when distilled alone, into carbon dioxide and cinnamene, C_8H_8 (p. 501).

The *cinnamates*, $C_9H_7O_2M$ (for monatomic metals), are very much like the benzoates. *Cinnyl cinnamate*, *Cinnamein*, or *Styracin*, $C_9H_7O_2.C_9H_9$, is contained, together with cinnamene and styrol, in liquid storax (which exudes from *Styrax calamita*, a shrub growing in Greece and Syria); also, together with styrol and other substances, in Peru and Tolu balsams, the produce of certain species of *Myroxylum* growing in South America. It is obtained from storax by distilling the balsam to expel the styrol, then boiling it with aqueous sodium carbonate to remove free cinnamic acid, and kneading the spongy residue between the fingers. Styracin then runs out as an oily liquid, and may be obtained in tufts of beautiful prisms by crystallization from alcohol. When distilled with potash, it is resolved into cinnyl alcohol and cinnamic acid.

Atropic Acid, $C_9H_8O_2$, is a crystalline acid, isomeric with cinnamic acid, obtained, together with a basic compound, *tropine*, by the action of alkalies on atropine, an alkaloïd existing in *Atropa Belladonna* and *Datura Stramonium*:

$C_{17}H_{23}NO_3$	=	$C_9H_8O_2$	+	$C_8H_{15}NO$
Atropine.		Atropic acid.		Tropine.

DIATOMIC ACIDS.

These acids are derived from diatomic alcohols by substitution either of O for H_2, in which case they contain three atoms of oxygen and are monobasic, or by substitution of O_2 for H_4, in which case they contain four atoms of oxygen and are bibasic.

The relation between the saturated hydrocarbons, the glycols, and the diatomic acids, is shown in the following table:

		Diatomic Acids.	
Hydrocarbons.	Glycols.	Monobasic.	Bibasic.
C_nH_{2n+2}	$C_nH_{2n+2}O_2$	$C_nH_{2n}O_3$	$C_nH_{2n-2}O_4$
C_nH_{2n}	$C_nH_{2n}O_2$	$C_nH_{2n-2}O_3$	$C_nH_{2n-4}O_4$
C_nH_{2n-2}	$C_nH_{2n-2}O_2$	$C_nH_{2n-4}O_3$	$C_nH_{2n-6}O_4$
C_nH_{2n-4}	$C_nH_{2n-4}O_2$	$C_nH_{2n-6}O_3$	$C_nH_{2n-8}O_4$.
	&c.	&c.	

Diatomic and Monobasic Acids.

1.—Lactic Series, $C_nH_{2n}O_3$.

The acids of this series may be divided into two groups, distinguished as *normal lactic acids* and *isolactic acids*. The known members of the series are:

Glycollic or Oxyacetic acid, $C_2H_4O_3$.
Lactic or Oxypropionic acid, $C_3H_6O_3$.
Oxybutyric acid, $C_4H_8O_3$, and its isomer, Dimethoxalic acid.
Oxyvaleric acid, $C_5H_{10}O_3$, and its isomer, Ethomethoxalic acid.
Leucic or Oxycaproic acid, $C_6H_{12}O_3$, and isomer, Diethoxalic acid.
Acids homologous with dimethoxalic acid, and containing 7, 9, and 12 atoms of carbon, have also been obtained.

The normal lactic acids correspond to the diatomic alcohols homologous with ethenic alcohol (glycol); thus:

$C_{n-1}H_{2n-2}OH$	$C_{n-1}H_{2n-2}OH$
$\vert$	$\vert$
CH_2OH	$COOH$
Diatomic alcohol.	Normal acid of lactic series.

If in the second formula we make n successively equal to 1, 2, 3, &c., we get the series:

OH	CH_2OH	C_2H_4OH	C_3H_6OH
$\vert$	$\vert$	$\vert$	$\vert$, &c.
$COOH$	$COOH$	$COOH$	$COOH$
Carbonic acid.	Glycollic acid.	Lactic acid.	Oxybutyric acid.

Carbonic acid is, however, a bibasic acid, for reasons which will be explained further on, and will be considered by itself.

The normal lactic acids are produced:

1. From the glycols by slow oxidation in contact with platinum black, or by the action of dilute nitric acid. The higher glycols, however, are partly split up by oxidation, part of their carbon as well as hydrogen being oxidized, and a lower acid of the series produced; thus amylene glycol yields oxybutyric instead of oxyvaleric acid.

2. By the action of moist silver oxide on the monochlorinated or monobrominated fatty acids (p. 708), *e. g.:*

$$\underset{\text{Chloropropionic acid.}}{C_3H_5ClO_2} + AgHO = AgCl + \underset{\text{Lactic acid.}}{C_3H_6O_3}$$

By the action of nitrous acid on the amidated derivatives of the fatty acids:

$$\underset{\text{Amidacetic acid (glycocine).}}{C_2H_5NO_2} + NO_2H = \underset{\text{Glycollic acid.}}{C_2H_4O_3} + OH_2 + N_2$$

The *Isolactic acids* are represented by the general formula, $\begin{matrix} C(C_nH_{2n+1})_2OH \\ \vert \\ COOH \end{matrix}$.

They are obtained in the form of ethers by the action of the zinc-compound of an alcohol-radical, C_nH_{2n+1}, on a neutral ether of oxalic acid containing a radical of the same series, such as diethylic oxalate. The reac-

tion consists in the replacement of an atom of oxygen in the oxalic ether by two equivalents of alcohol-radical, and the simultaneous replacement of an equivalent of ethyl, methyl, &c., in the oxalic ether by an equivalent * of zinc, whereby an ether of zinc-diethyloxalic acid, &c., is produced, which by certain obvious transformations may be converted into the required acid; thus:

$$\underset{\text{Dimethylic oxalate.}}{\begin{matrix}COOCH_3\\ |\\ COOCH_3\end{matrix}} + \underset{\text{Zinc methide.}}{2Zn'C_2H_5} = \underset{\text{Zinc methylate.}}{Zn'(CH_3)O} + \underset{\text{Methylic zinco-diethoxalate.}}{\begin{matrix}C(C_2H_5)_2OZn'\\ |\\ COOCH_3\end{matrix}}$$

$$\underset{\text{Methylic zinco-diethoxalate.}}{\begin{matrix}C(C_2H_5)_2OZn'\\ |\\ COOCH_3\end{matrix}} + \underset{\text{Water.}}{HOH} = \underset{\text{Zinc hydrate.}}{Zn'HO} + \underset{\text{Methylic diethoxalate.}}{\begin{matrix}C(C_2H_5)_2OH\\ |\\ COOCH_3\end{matrix}}$$

The methylic diethoxalate is easily decomposed by baryta-water, yielding methyl alcohol and barium diethoxalate:

$$\underset{\text{Methylic diethoxalate.}}{\begin{matrix}C(C_2H_5)_2OH\\ |\\ COOCH_3\end{matrix}} + Ba'HO = CH_3(OH) + \underset{\text{Barium diethoxalate.}}{\begin{matrix}C(C_2H_5)_2OH\\ |\\ COOBa'\end{matrix}}$$

And this salt decomposed by sulphuric acid yields diethoxalic acid, $\begin{matrix}C(C_2H_5)_2OH\\ |\\ COOH\end{matrix}$, isomeric with leucic acid.

In the first stage of the process it is found best to use a mixture of ethyl iodide with metallic zinc, which produces zinc-ethide, instead of the latter compound previously prepared. The other isolactic ethers are prepared in a similar manner.

The acids of either group are reduced by hydriodic acid to the corresponding acids of the acetic series; *e. g.:*

$$\underset{\text{Lactic acid.}}{C_3H_6O_3} + 2HI = \underset{\text{Propionic acid.}}{C_3H_6O_2} + OH_2 + I_2$$

The ethereal salts of the isolactic acids are converted by phosphorus trichloride or pentoxide, into ethers of the iso-acrylic acids (p. 625); the ethereal salts of the normal lactic acids do not exhibit this reaction.

The normal lactic acids, when heated, give up a molecule of water, and are converted into oxygen ethers or anhydrides; *e. g.:*

$$\underset{\text{Lactic acid.}}{C_3H_6O_3} - OH_2 = \underset{\text{Lactide.}}{C_3H_4O_2}$$

Two molecules of a normal lactic acid may also be deprived of a molecule of water, thereby producing a condensed acid, analogous to the polyethenic alcohols; *e. g.:*

$$\underset{\text{Lactic acid.}}{2C_3H_6O_3} - OH_2 = \underset{\text{Dilactic acid.}}{CH_{610}O_5}$$

* To simplify the equations, we have made use of the *equivalent* (32·5) instead of the atom (65) of zinc, denoting it by the symbol Zn'.

Glycollic Acid, $C_2H_4O_3 = \begin{matrix} CH_2OH \\ | \\ COOH \end{matrix}$.—This acid is produced in a variety of reactions, several of which have been already mentioned, viz., the oxidation of glycol by contact with platinum black or by treatment with dilute nitric acid; the decomposition of benzoglycollic acid by boiling with water; the decomposition of glycocine by nitrous acid; the action of water or alkalies on bromacetic and chloracetic acid, or their salts (pp. 603, 614, 638), *e. g.*, by boiling silver bromacetate with water:

$$C_2H_2BrAgO_2 + OH_2 = AgBr + C_2H_4O_3$$

It is also produced: *a.* By the action of alkalies on glyoxal and glyoxylic acid:

$$\underset{\text{Glyoxal.}}{C_2H_2O_2} + OH_2 = \underset{\text{Glycollic acid.}}{C_2H_4O_3}$$

$$\underset{\text{Glyoxylic acid.}}{2C_2H_4O_4} = \underset{\text{Oxalic acid.}}{C_2H_2O_4} + \underset{\text{Glycollic acid.}}{C_2H_4O_3} + OH_2.$$

β. Together with glyoxal, glyoxylic acid, and other products by the action of nitric acid upon alcohol.

γ. By the action of nascent hydrogen (evolved by zinc and sulphuric acid) upon oxalic acid:

$$\underset{\text{Oxalic acid.}}{C_2H_2O_4} + 2H_2 = OH_2 + \underset{\text{Glycollic acid.}}{C_2H_4O_3}$$

Glycollic acid differs somewhat in its properties, according to the manner in which it is prepared, being sometimes syrupy and uncrystallizable, sometimes separating from its solution in ether in large regular crystals. It has a very sour taste, dissolves easily in water, alcohol, and ether; melts at 78° or 79° C. (172°–174° F.); begins to boil at 100°; decomposes when heated to above 150° C. (302° F.). All the glycollates are more or less soluble and crystallizable.

Diglycollic acid, $C_4H_6O_5 = 2C_2H_4O_3 - OH_2$, also called *Paramalic acid.*—This acid, isomeric with malic acid, and related to glycollic acid in the same manner as diethenic alcohol to glycol, is produced by the dehydration of glycollic acid, and by the oxidation of diethenic or triethenic alcohol. It is also formed in the preparation of glycollic acid by heating sodium chloracetate with caustic soda, which in fact is the process by which it was first obtained:

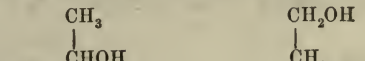
$$\underset{\text{Chloracetic acid.}}{C_2H_3ClO_2} + 2NaHO = NaCl + OH_2 + \underset{\text{Sodium glycollate.}}{C_2H_3NaO_3}$$

$$\underset{\text{Chloracetic acid.}}{C_2H_3ClO_2} + \underset{\text{Sodium glycollate.}}{C_2H_3NaO_3} = NaCl + \underset{\text{Diglycollic acid.}}{C_4H_6O_5}$$

Diglycollic acid is a crystalline bibasic acid, forming with univalent metals, normal salts containing $C_4H_5M'O_5$, and acid salts, $C_4H_4M_2O_5$; with bivalent metals it forms only normal salts, $C_4H_4M''O_5$.

Lactic Acid, $C_3H_6O_3 = \begin{matrix} C_2H_4OH \\ | \\ COOH \end{matrix}$ or $C\begin{cases} HC_2H_4OH \\ O'' \\ OH \end{cases}$.—Of this acid there are two modifications: one called *ordinary lactic acid*, produced by a peculiar fermentation of sugar; the second, called *paralactic* or *sarcolactic acid*,

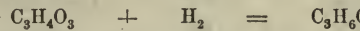
existing in muscular flesh. The difference of constitution between these two acids is represented by the following formulæ:



Ordinary lactic acid. Paralactic acid.

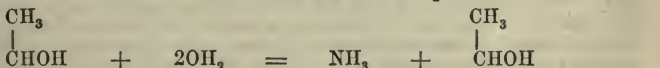
Ordinary lactic acid is also produced by the first three general methods given on page 642, viz., by the slow oxidation of propene glycol; by the action of moist silver oxide on chloro-propionic or bromo-propionic acid; and by the action of nitrous acid on alanine; further, by the following special processes:

a. By the action of nascent hydrogen on pyruvic acid:



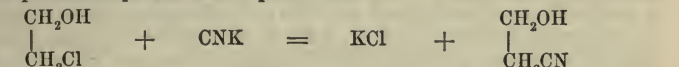
β. By the action of hydrocyanic acid and water on acetic aldehyde:

Aldehyde. Hydrocyanic acid. Unknown intermediate compound.

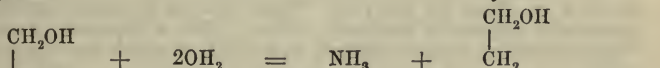


Intermediate compound. Lactic acid.

Paralactic acid is produced:—1. By heating ethene chlorohydrate with an alcoholic solution of potassium cyanide, and boiling the resulting ethene cyano-hydrate with caustic potash, whereupon ammonia is given off, and potassium paralactate is produced:

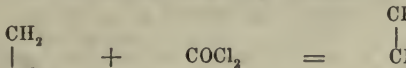


Ethene chlorhydrate. Ethene cyanohydrate.



Ethene cyanohydrate. Paralactic acid.

2. By combining ethene with carbonyl chloride, whereby paralactyl chloride is produced, and decomposing this chloride with an alkali:



Ethene. Paralactyl chloride.

$$\begin{array}{ccccccc} CH_2Cl & & & & & & CH_2OH \\ | & & & & & & | \\ CH_2 & + & 2HOH & = & 2HCl & + & CH_2 \\ | & & & & & & | \\ COCl & & & & & & COOH \end{array}$$

Paralactyl chloride. Paralactic acid.

Paralactic acid is extracted from muscular flesh by cold water or dilute alcohol.

Preparation of ordinary lactic acid by Fermentation.—Various kinds of sugar, and dextrin, when subjected to the action of particular ferments, are converted into lactic acid, the change consisting in a resolution of the molecule, preceded in some cases by the assumption of the elements of water:

$$\begin{array}{ccc} C_6H_{12}O_6 & = & 2C_3H_6O_3 \\ \text{Glucose.} & & \text{Lactic acid.} \end{array}$$

$$\begin{array}{ccccc} C_{12}H_{22}O_{11} & + & OH_2 & + & 4C_3H_6O_3 \\ \text{Milk sugar.} & & & & \text{Lactic acid.} \end{array}$$

This lactous fermentation requires a temperature between 20° and 40° C. (58° and 104° F.), and the presence of water and certain ferments—viz., albuminous substances in a peculiar state of decomposition, such as casein, glutin, or animal membranes, especially the coating of the stomach of the calf (rennet), or of the dog, or bladder. According to Pasteur and others, it depends upon the presence of a peculiar fungus, *Penicillium glaucum* (p. 521). The following is a good method for preparing the acid in considerable quantity: 2 gallons of milk are mixed with 6 pounds of raw sugar, 12 pints of water, 8 ounces of putrid cheese, and 4 pounds of chalk, which should be mixed up to a creamy consistence with some of the liquid. This mixture is exposed in a loosely covered jar to a temperature of about 30° C. (86° F.), with occasional stirring. The use of the chalk is to neutralize the lactic acid, which would otherwise coagulate the casein, render it insoluble, and thereby put a stop to the process. At the end of two or three weeks it will be found converted into a semi-solid mass of calcium lactate, which may be drained, pressed, and purified by re-crystallization from water. The lactate may be decomposed by the necessary quantity of pure oxalic acid, the filtered liquor neutralized with zinc carbonate, and, after a second filtration, evaporated until the zinc-salt crystallizes out on cooling. An important modification of this process consists in employing commercial zinc-white instead of powdered chalk, which yields at once difficultly soluble zinc lactate, easily purified by re-crystallization. The zinc lactate may, lastly, be re-dissolved in water, and decomposed by sulphuretted hydrogen, in order to obtain the free acid. Together with the lactic acid a certain quantity of mannite is invariably formed. This is separated by agitating the concentrated aqueous solution with ether, in which lactic acid alone is soluble.

If, in the first part of the process, the solid calcium lactate be not removed at the proper time from the fermenting liquid, it will gradually re-dissolve and disappear, being converted into soluble butyrate (p. 617).

Lactic acid may be extracted from a great variety of liquids containing decomposing organic matter, as *sauerkraut*, a preparation of white cabbage, the sour liquor of the starch-maker, &c.

Solution of lactic acid may be concentrated in the vacuum of the air-pump, over a surface of oil of vitriol, until it appears as a colorless, syrupy liquid, of sp. gr. 1·215. It has an intensely sour taste and acid reaction: it is hygroscopic, and very soluble in water, alcohol, and ether. All its salts are soluble.

When syrupy lactic acid is heated in a retort to 130° C. (266° F.), water

containing a little lactic acid distils over, and the residue on cooling forms a yellowish, solid, fusible mass, very bitter, and nearly insoluble in water. This is *dilactic acid*, $C_6H_{10}O_5 = 2C_3H_6O_3 - OH_2$. Long-continued boiling with water re-converts it into lactic acid. When this substance is further heated, it decomposes, yielding numerous products. One of these is *lactide*, or lactic anhydride, $C_3H_4O_2$, a volatile substance, crystallizing in brilliant, colorless, rhombic plates, which, when put into water, slowly dissolve, with production of lactic acid.

Lactide combines with *ammonia*, forming *lactamide*, a soluble crystallizable substance isomeric with alanine or amidopropionic acid (p. 615). The difference between these two bodies and their relation to lactic acid is exhibited by the following formulæ:

$C_2H_4NH_2$	C_2H_4OH	C_2H_4OH
COOH	COOH	$CONH_2$
Alanine.	Lactic acid.	Lactamide.

Alanine may be derived from lactic acid by substitution of amidogen for the *alcoholic* hydroxyl of the acid (which comes to exactly the same thing as replacing an atom of hydrogen in propionic acid, $C_3H_6O_2$, by amidogen); accordingly it retains an atom of basic hydrogen, and therefore reacts as an acid (lactamic or amidopropionic acid); but in lactamide the *basic* hydroxyl is replaced by amidogen, and therefore the compound is neutral.

Another product of the action of heat on lactic acid is *lactone*, a colorless volatile liquid, boiling at 92·2° C. (198° F.). Acetone is also formed, and carbon monoxide and dioxide are given off. Lactic acid, boiled with dilute nitric acid, or with dioxide of lead or barium, is converted into oxalic acid. Distilled with dilute sulphuric acid and dioxide of lead or manganese, it yields a large quantity of aldehyde, together with carbon dioxide. Hydriodic acid, or a mixture of phosphorus tetroxide and water, reduces it to propionic acid, with liberation of iodine:

$$C_3H_6O_3 + 2HI = C_3H_6O_2 + OH_2 + I_2.$$

Paralactic acid in solution or in the syrupy state is undistinguishable from ordinary lactic acid. When heated it is converted into lactide, which, when boiled with water, yields ordinary lactic acid.

Lactates. — The best defined of these salts are represented by the formulæ, $C_3H_5O_3M'$, and $(C_3H_5O_3)_2M''$. Barium and calcium also form acid lactates, *e. g.*, $(C_3H_5O_3)_2Ca'' . 2C_3H_6O_3$. The lactates are, for the most part, sparingly soluble in cold water, and effloresce rapidly from their solutions: they are all insoluble in ether. When heated with excess of strong sulphuric acid, they give off a large quantity of pure carbon monoxide,

The paralactates have, for the most part, the same composition as the lactates; but some of them differ in form, solubility, and other characters.

Calcium lactate, $(C_3H_5O_3)_2Ca'' . 5$ Aq., is obtained in the fermentation process above described, or by boiling aqueous lactic acid with calcium carbonate. It dissolves in 9·5 parts of water at ordinary temperatures. The paralactate contains only 4 molecules of water, which however it retains longer than the lactate, and requires 12 parts of water to dissolve it. — *Zinc lactate*, $(C_3H_5O_3)_2Zn'' . 3$ Aq., gives off its water quickly at 100°, dissolves in 6 parts of boiling water, in 5·8 parts of cold water, and is nearly insoluble in alcohol. The paralactate contains only 2 molecules of crystallization-water, which it retains with considerable force. It dissolves in 2·88 parts of boiling, 5·7 parts of cold water, and in 2·23 parts of alcohol, either cold or boiling. — *Ferrous lactate* is precipitated in small yellowish needles on mixing ammonium lactate with ferrous chloride or sulphate. — *Ferric lactate* is a brown deliquescent mass.

Lactic Ethers. — Lactic acid, like the other members of the group, can form three different ethers containing the same univalent alcohol-radical, according as the alcoholic or the basic hydrogen-atom, or both, are replaced; thus:

C_2H_4OH	$C_2H_4OC_2H_5$	C_2H_4OH	$C_2H_4OC_2H_5$
$COOH$	$COOH$	$COOC_2H_5$	$COOC_2H_5$
Lactic acid.	Ethyl-lactic acid.	Monethylic lactate.	Diethylic lactate, or ethylic ethyl lactate.

Monethylic lactate, $C_3H_5O_4 . C_2H_5$, is produced by distilling potassium or sodium lactate with potassium ethylsulphate. It is a syrupy liquid, boiling at 176° C. (348° F.). Potassium dissolves in it, with evolution of hydrogen, forming *ethylic potassio-lactate,* $\begin{matrix} C_2H_4OK \\ | \\ COC_2H_5 \end{matrix}$. — *Ethyl-lactic acid,* $C_3H_4(C_2H_5)O_3.H$, is obtained as a potassium or calcium-salt by decomposing diethylic lactate with potash or milk of lime. When separated from these salts by sulphuric acid, it forms a viscid liquid, boiling with partial decomposition between 195° and 198° C. (383°–388° F.). *Diethylic lactate,* $C_3H_4(C_2H_5)O_3 . C_2H_5$, is produced by the action of ethyl-iodide on ethylic potassio-lactate, or on sodium ethylate, and by that of sodium ethylate on ethyl-chloropropionate:

$C_3H_4ClO . C_2H_5$	+	C_2H_5ONa	=	$NaCl$	+	$C_3H_4O_3 . (C_2H_5)_2$
Ethyl-chloro-propionate.		Sodium ethylate.				Diethylic lactate.

Methyllactic acid, $C_3H_4(CH_3)O_3(OH)$, and its zinc and silver salts have also been obtained.

The alcoholic hydrogen of lactic acid may also be replaced by acid radicals, forming such compounds as *acetolactic acid,* $C_3H_4(C_2H_3O)O_2 . OH$.

Lactyl Chloride, $C_3H_4OCl_2$, or Chloropropionyl Chloride, $C_3H_4ClO . Cl$, is obtained, together with phosphorus oxychloride, by gently heating a mixture of calcium lactate with phosphorus pentachloride; also by the direct combination of ethene with carbonyl chloride. It is a colorless liquid, boiling above 100°, and decomposed with water, forming hydrochloric and chloropropionic acids.

Leucic Acid, $C_6H_{12}O_3 = \begin{matrix} C_5H_{10}OH \\ | \\ COOH \end{matrix}$. — This acid, isomeric with diethoxalic acid, is produced by the action of nitrous acid on leucine or amidocaproic acid (p. 619). It forms needles or monoclinic prisms, soluble in water, alcohol, and ether, melting at about 73° C. (163° F.), and volatilizing at 100°. When heated for some time at that temperature, it gives off water, and leaves a syrupy oxide or anhydride. It forms crystallizable salts analogous to the lactates.

Carbonic Acid, $CH_2O_3 = C\begin{cases} OH \\ O'' \\ OH \end{cases}$. — This acid belongs to the lactic series, so far as its constitution is concerned, being derived from the unknown methane glycol, $C\begin{cases} OH \\ H_2 \\ OH \end{cases}$, by substitution of O for H_2; but it differs from all

the other acids of the series in being bibasic, both the hydroxyl groups contained in it being immediately connected with an atom of oxygen, so that either of the hydrogen-atoms may be regarded as belonging to the group CO_2H.

Carbonic acid itself, or hydrogen carbonate, is not known, inasmuch as when a metallic carbonate is decomposed by a stronger acid, the hydrogen carbonate, CH_2O_3, always splits up into water and carbon dioxide, which escapes as gas. The corresponding sulphur-compound, CH_2S_3, is, however, obtained as an oily liquid when a metallic sulpho-carbonate is decomposed by an acid (p. 203).

With the alkali-metals carbonic acid forms acid and normal or neutral salts, according as one or both of the hydrogen-atoms are replaced; *e. g.*:

Acid sodium carbonate, $CHNaO_3$, or $CO\begin{cases}OH\\ONa\end{cases}$

Normal sodium carbonate, CNa_2O_3, or $CO(ONa)_2$.

With the earth-metals and other dyad metals, carbonic acid forms only normal salts, $CM''O_3$, and basic salts; the so-called acid carbonates of barium, calcium, &c., are known only in solution, and are, in fact, merely solutions of neutral carbonates in aqueous carbonic acid, which give off carbon dioxide on boiling. The basic carbonates of dyad metals may be viewed as compounds of normal carbonates with metallic oxides or hydrates; for example, slaked lime, produced by exposing quicklime to moist air, has the composition of a dicalcic carbonate, $Ca''O . CO_3Ca''$. Aq.; and native green copper carbonate, or malachite, consists of $Cu''O . CO_3Cu''$. Aq. These basic carbonates may, however, be viewed in another way, namely, as derived from a tetratomic carbonic acid, or *orthocarbonic acid*, CH_4O_4, or $C(OH)_4$, analogous to methane and carbon tetrachloride; thus, dicalcic carbonate $= CCa''_2O_4 . Aq.$; malachite $= CCu''_2O_4 . Aq.$

With metals of higher atomicity, carbonic acid does not form definite salts.

Carbonic Ethers. — The only carbonic ethers known are those in which the two hydrogen-atoms of carbonic acid are replaced either by two equivalents of a monad alcohol-radical, or by one equivalent of a monad alcohol-radical and one equivalent of a metal.

Ethyl carbonate, $CO_3(C_2H_5)_2$, is formed by the action of ethyl iodide on silver carbonate:

$$CO_3Ag_2 + 2C_2H_5I = 2AgI + CO_3(C_2H_5)_2;$$

also by the action of potassium or sodium on ethyl oxalate, $C_2O_4(C_2H_5)_2$: this reaction is not quite understood; but it amounts to the removal of carbon monoxide, or carbonyl, CO, from the oxalic ether. Fragments of potassium or sodium are dropped into oxalic ether as long as gas is disengaged: the brown pasty product is then mixed with water and distilled. The carbonic ether is found floating upon the surface of the water of the receiver as a colorless, limpid liquid of aromatic odor and burning taste. It boils at 125° C. (257° F.), and is decomposed by an alcoholic solution of potash into potassium carbonate and alcohol. By chlorine in diffused daylight it is converted into tetrachlorethyl carbonate, $CO_3 . (C_2H_3Cl_2)_2$, and in sunshine into pentachlorethyl carbonate, $CO_3(C_2Cl_5)_2$.

Ethyl-potassium carbonate, $CO_3(C_2H_5)K$, is produced by passing carbonic acid gas into a cooled solution of potassium hydrate in absolute alcohol:

$$C_2H_6O + KHO + CO_2 = OH_2 + CO_3 . (C_2H_5)K.$$

It is a white nacreous salt, decomposed by water into potassium carbonate and alcohol.

Ethyl-methyl carbonate, $CO_3(C_2H_5)(CH_3)$, is obtained by distilling a mixture of ethyl-potassium sulphate and methyl-potassium carbonate:

$$SO_4 \cdot (C_2H_5)K + CO_3 \cdot (CH_3)K = SO_4K_2 + CO_3(C_2H_5)(CH_3).$$

Methyl-barium carbonate, $(CO_3)_2(CH_3)_2Ba''$, is obtained as a white precipitate by passing carbonic acid gas into a solution of baryta in methyl alcohol.

Carbonates of *butyl*, *amyl*, and *allyl*, analogous in composition to ethyl carbonate, have also been obtained. *Phenyl hydrogen carbonate*, or *acid phenyl carbonate*, $CO_3(C_6H_5)H$, is identical with salicylic acid, which will be described further on.

Ethyl orthocarbonate,* $C(OC_2H_5)_4$, is produced by heating a mixture of chloropicrin (trichloro-nitromethane) with absolute alcohol and sodium:

$C(NO_2)Cl_3$	+	$4C_2H_5NaO$	=	$3NaCl$	+ NO_2Na	+ $C(OC_2H_5)_4$
Chloropicrin.		Sodium ethylate.		Sodium chloride.	Sodium nitrile.	Ethyl ortho-carbonate.

It is a colorless oil, boiling at 158°–159° C. (313°–318° F.). Heated with boric oxide to 100°, it is resolved into ethyl anhydroborate (p. 528), and ordinary ethyl carbonate:

$$C(OC_2H_5)_4 + 2B_2O_3 = 2BO_2C_2H_5 \cdot B_2O_3 + CO_3(C_2H_5)_2.$$

Sulphocarbonic Ethers. — These are bodies having the composition of carbonic ethers in which the oxygen is replaced, wholly or partly, by sulphur. The following table exhibits their names and formulæ, the ethyl and ethene compounds being taken as examples:

Ethyl-monosulphocarbonic acid . . .	$CO_2S \cdot (C_2H_5)H$.
Diethylic monosulphocarbonate . . .	$CO_2S \cdot (C_2H_5)_2$.
Ethyl-disulphocarbonic or Xanthic acid .	$COS_2 \cdot (C_2H_5)H$.
Diethylic disulphocarbonate . . .	$COS_2 \cdot (C_2H_5)_2$.
Ethyl-trisulphocarbonic acid . . .	$CS_3 \cdot (C_2H_5)H$.
Diethylic trisulphocarbonate . . .	$CS_3 \cdot (C_2H_5)_2$.
Ethene disulphocarbonate	$COS_2 \cdot (C_2H_4)''$.
Ethene trisulphocarbonate	$CS_3 \cdot (C_2H_4)''$.

The metallic salts of the *acid sulphocarbonic ethers* are produced in the same manner as those of the carbonic ethers: thus carbonic dioxide unites with potassium sulphethylate (mercaptide), to form potassium ethyl-monosulphocarbonate, just as it unites with potassium ethylate to form the ethyl-carbonate; and, in like manner, carbon disulphide acts on potassium ethylate or alcoholic potash, so as to form potassium ethyldisulphocarbonate; and on potassium mercaptide, or an alcoholic solution of the sulphhydrate, so as to form the ethyltrisulphocarbonate, thus:

CO_2	+ $(C_2H_5)KO$	= $CO_3(C_2H_5)K$	Ethylcarbonate.
CO_2	+ $(C_2H_5)KS$	= $CO_2S(C_2H_5)K$	Ethylmonosulphocarbonate.
CS_2	+ $(C_2H_5)KO$	= $COS_2(C_2H_5)K$	Ethyldisulphocarbonate.
CS_2	+ $(C_2H_5)KS$	= $CS_3(C_2H_5)K$	Ethyltrisulphocarbonate.

The *neutral sulphocarbonic ethers* (containing monatomic alcohol-radicals) are produced by the action of the chlorides, bromides, &c. of alcohol-radicals on the metallic salts of the corresponding acid ethers, *e. g.*:

$(C_2H_5)KCS_3$	+ C_2H_5Cl	= KCl	+	$(C_2H_5)_2CS_3$	
Potassic ethyl-trisulphocarbonate.				Ethylic trisul-phocarbonate.	

* *H. Bassett*, Chem. Soc. Journal [2], i. 198.

The sulphocarbonic ethers of diatomic alcohol-radicals are formed by the action of diatomic alcoholic bromides, iodides, &c., on sodium sulphocarbonate, *e. g.*:

$$\underset{\text{Ethene bromide.}}{C_2H_4Br_2} + CS_3Na_2 = 2NaBr + \underset{\text{Ethene tri-sulphocarbonate.}}{CS_3(C_2H_4)''}$$

The neutral sulphocarbonic ethers are oily liquids; so likewise are the acid ethers, such at least as are known in the free state, or as hydrogen-salts; their metallic salts are mostly crystalline. The best known of these compounds are the *ethyldisulphocarbonates* or *xanthates*.

To prepare *xanthic acid*, alcohol of 0·800 sp. gr. is saturated, whilst boiling, with potash, and into this solution carbon bisulphide is dropped till it ceases to be dissolved, or until the liquid loses its alkalinity. On cooling the whole to —18° C. (0° F.), the potassium-salt separates in the form of brilliant, slender, colorless prisms, which must be quickly pressed between folds of bibulous paper, and dried in a vacuum. It is freely soluble in water and alcohol, but insoluble in ether, and is gradually destroyed by exposure to air, by oxidation of part of the sulphur. Xanthic acid may be prepared by decomposing this salt with dilute sulphuric or hydrochloric acid. It is a colorless, oily liquid, heavier than water, of powerful and peculiar odor, and very combustible: it reddens litmus-paper, and ultimately bleaches it. Exposed to gentle heat (about 24° C. [75° F.]), it is decomposed into alcohol and carbon bisulphide. Exposed to the air, or kept beneath the surface of water open to the air, it becomes covered with a whitish crust, and is gradually destroyed. The xanthates of the alkali-metals and of barium are colorless and crystallizable; the calcium-salt dries up to a gummy mass; the xanthates of zinc, lead, and mercury are white, and but slightly soluble; that of copper is a flocculent, insoluble substance, of beautiful yellow color.

Ethylic disulphocarbonate or *Xanthic ether*, $COS_2 . (C_2H_5)_2$, obtained by the action of ethyl chloride on potassium xanthate, is a pale-yellow oil, boiling at 200° C. (392° F.), insoluble in water, soluble in all proportions of alcohol or ether. Ammonia-gas passed into its alcoholic solution forms mercaptan and a crystalline substance called *xanthamide*:

$$\underset{\text{Xanthic ether.}}{COS_2(C_2H_5)_2} + NH_3 = \underset{\text{Mercaptan.}}{C_2H_5(SH)} + \underset{\text{Xanthamide.}}{COS(C_2H_5)NH_2}$$

Amyl-disulphocarbonate, $COS(C_5H_{11})_2$, treated in like manner, yields *xanthamylamide*, $COS(C_5H_{11})NH_2$.

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2. — Pyruvic Series, $C_nH_{2n-2}O_3$.

This is a small group of acids, including —

Pyruvic acid, $C_3H_4O_3$	Jalapinoleic acid, $C_{16}H_{30}O_3$?
Convolvulinoleic acid, $C_{13}H_{24}O_3$?	Ricinoleic acid, $C_{18}H_{34}O_3$.

Glyoxylic acid, a product of the oxidation of alcohol, glycol, and glyoxal, is sometimes said to have the composition $C_2H_2O_3$; but it is more probably $C_2H_4O_4$, and belongs to another series, as will be explained hereafter.

Pyruvic Acid, $C_3H_4O_3$, also called *Pyroracemic acid*, is produced by dry distillation of racemic or tartaric acid:

$$C_4H_6O_6 = C_3H_4O_3 + CO_2 + OH_2.$$

It is a liquid, boiling, with partial decomposition, at about 165° C. (329° F.). Treated with sodium amalgam, or hydriodic acid, it takes up two atoms of hydrogen, and is converted into lactic acid, $C_3H_6O_3$, or if the reagent is used in large excess, into propionic acid, $C_3H_6O_2$. It also unites directly with bromine, forming the acid, $C_3H_4Br_2O_3$, probably dibromolactic acid. Its salts crystallize readily.

Convolvulinoleic Acid and **Jalapinoleic Acid**, are produced by the action of acids or alkalies from certain resinous glucosides contained in the root of tuberose or officinal jalap (*Convolvulus Schiedanus*), and of *Convolvulus* (or *Ipomœa*) *orizabensis*, the jalap-stalks or jalap-wood of commerce; but their formulæ have not been exactly determined.

Ricinoleic Acid, $C_{18}H_{34}O_3$, is a yellow oily acid, produced by the saponification of castor-oil. At temperatures between —6° and —7° C° (19°–21° F.), it solidifies to a granular mass. The neutral ricinoleates of the alkali-metals when distilled alone yield a distillate of œnanthol; but when distilled with excess of caustic alkali, they give off hydrogen, and yield a distillate of octyl alcohol, $C_8H_{18}O$, and a residue of alkaline sebate, $C_{10}H_{16}K_2O_4$ (p. 541).

3.—Series $C_nH_{2n-4}O_3$.

The only known acid of this series is *guaiacic acid*, $C_6H_8O_3$, which is a crystallizable substance contained in guaiacum, a resin obtained from *Guaiacum officinale*, a tree growing in Jamaica. It sublimes in needles resembling benzoic acid, and is resolved by dry distillation into carbon dioxide and guaiacene, C_5H_8O.

4.—Series $C_nH_{2n-8}O_3$.

This series includes the following acids, related to the aromatic acids in the same manner as the lactic acids are related to the fatty acids:

Oxybenzoic, Para-oxybenzoic, and Salicylic acids . .	$C_7H_6O_3$
Formobenzoic, Creosotic, Carbocresylic, and Anisic acids	$C_8H_8O_3$
Phloretic acid	$C_9H_{10}O_3$
Thymotic and Thymyl-carbonic acids	$C_{11}H_{14}O_3$

Oxybenzoic Acid, $C_7H_6O_3$, or $C_6H_4(OH).CO_2H$, is produced by the action of nitrous acid on amidobenzoic acid:

$$\underset{\text{Amidobenzoic acid.}}{C_6H_4(NH_2).CO_2H} + NO(OH) = \underset{\text{Oxy-benzoic acid.}}{C_6H_4(OH).CO_2H} + OH_2 + N_2.$$

Oxybenzoic acid is only slightly soluble in cold water or alcohol, but dissolves easily in either of these liquids at the boiling heat, and separates as a crystalline powder on cooling. At higher temperatures it melts and sublimes without decomposition, a character by which it is distinguished from its two isomers. With strong nitric acid it forms nitro-oxybenzoic acid, $C_7H_5(NO_2)O_3$, which is converted by ammonium sulphide into amid-oxybenzoic acid, $C_7H_5(NH_2)O_3$.

Para-oxybenzoic Acid is produced by heating anisic acid to 125°–130° with strong hydriodic acid:

$$C_8H_8O_3 + HI = CH_3I + C_7H_6O_3.$$

It is more soluble in cold water than oxybenzoic acid, dissolving in 126 parts of water at 15°: from a hot solution it crystallizes in small distinct monoclinic prisms. It melts with partial decomposition at 210° C. (410° F.), and is easily resolved at higher temperatures into carbon dioxide and phenol:

$$C_7H_6O_3 = CO_2 + C_6H_6O.$$

Its solution forms, with ferric chloride, a yellow precipitate insoluble in excess, without violent coloration. These characters distinguish it from oxybenzoic acid. With most metals it reacts like a monobasic acid, its potassium-salt containing $C_7H_5O_3K$, and its cadmium-salt $(C_7H_5O_3)_2Cd''$; but it appears also, like salicylic acid, to form a barium-salt containing $C_7H_4Ba''O_3$.

Salicylic Acid is produced: 1. By passing carbon dioxide into phenol containing small pieces of sodium:

$$NaOC_6H_5 + CO_2 = (CO)''\begin{cases} OC_6H_5 \\ ONa \end{cases}$$

Sodium phenate. Sodium salicylate.

2. From salicylol, $C_7H_6O_2$, by oxidation with aqueous chromic acid, or by melting salicylol or salicin with potassium hydrate, in which case hydrogen is evolved:

$$\underset{\text{Salicylol.}}{C_7H_6O_2} + KOH = \underset{\substack{\text{Potassium} \\ \text{salicylate.}}}{C_7H_5O_3K} + H_2.$$

3. Coumaric acid, heated with potassium hydrate, yields potassium salicylate and acetate:

$$C_9H_8O_3 + 2KOH = C_7H_5O_3K + C_2H_3O_2K + H_2.$$

4. Oil of wintergreen (*Gaultheria procumbens*), which consists of methylsalicylic acid, is resolved, by distillation with potash, into methyl alcohol and salicylic acid:

$$C_7H_5(CH_3)O_3 + KOH = CH_3(OH) + C_7H_5KO_3.$$

Salicylic acid crystallizes from its alcoholic solution by spontaneous evaporation in large monoclinic prisms. It requires about 1000 parts of cold water to dissolve it, but is much more soluble in hot water and in alcohol. Its aqueous solution imparts a deep violet color to ferric salts. It melts at 130° C. (266° F.), gives off phenol at a higher temperature, and when heated with pounded glass or quicklime, is completely resolved into carbon dioxide and phenol. It is distinguished from both its isomers by its behavior with ferric salts, its very slight solubility in water, and its lower melting point: it differs from oxybenzoic acid by its behavior when heated.

In its relations to metals, salicylic acid appears to be intermediate between monobasic and bibasic acids. With the alkali-metals and silver, it forms only acid salts like $C_7H_5KO_3$; but with dyad metals it forms both acid and neutral salts; with calcium, for example, the two salts, $C_7H_4Ca''O_3$ and $C_{14}H_{10}Ca''O_6$, or $(C_7H_5O_3)_2Ca''$. The neutral salts are, however, much less easily formed than the acid salts, being produced only in presence of a large excess of base. Its formation from carbon dioxide and phenol seems to show that it may be regarded as acid phenyl carbonate, $(CO)''(OC_6H_5)(OH)$; and in the neutral salicylates of bivalent metals, such as $C_7H_4Ca''O_3$, the metal appears to replace one atom of hydrogen from the group OH, and another from the group OC_6H_5.*

* *Piria*, Ann. Ch. Pharm. xciii. 262.

Salicylic acid forms both acid and neutral ethers. Oil of wintergreen, as already observed, consists of methyl-salicylic acid, $C_7H_5(CH_3)O_3$. A similar compound, containing ethyl, is obtained by distilling crystallized salicylic acid with alcohol and sulphuric acid These compounds are monobasic acids, the basic hydrogen of which may be replaced by metals or by alcoholic-radicals, forming neutral salicylic ethers, such as $C_7H_4(CH_3)_2O_3$, $C_7H_4(CH_3)(C_2H_5)O_3$, &c. There is also an ethene-salicylic acid, $C_{14}H_{10}(C_2H_4)''O_6$, consisting of a double molecule of salicylic acid with two hydrogen-atoms replaced by ethene; it is produced by heating ethene-bromide with silver salicylate.

Carbocresylic and Cresotic Acids,* $C_8H_8O_3$. — The sodium-salts of these acids are formed simultaneously by the action of carbon dioxide and sodium on cresol, C_7H_8O. On treating the product with hydrochloric acid, the carbocresylic acid is resolved into carbonic dioxide and cresol, while the cresotic acid remains undecomposed, and may be washed out with ammonium carbonate; the solution, on evaporation, yielding the cresotic acid in fine large prisms which melt at 153° C. (307° F.), are slightly soluble in water, easily in alcohol and ether. It forms a deep violet color with ferric chloride. When heated with causic baryta, it is resolved into carbon dioxide and cresol. With regard to their comparative facility of decomposition, carbocresylic and cresotic acids appear to be related to one another, in the same manner as salicylic and oxybenzoic acids.

Formobenzoic Acid, $C_8H_8O_3$, is produced by evaporating crude bitter-almond oil to dryness with hydrochloric acid, and exhausting the residue with ether, which leaves sal-ammoniac undissolved. It contains the elements of benzoic acid, $C_7H_6O_2$, and formic acid, CH_2O_2, minus an atom of oxygen; and its formation appears to be due to the action of the hydrochloric acid on the hydrocyanic acid of the crude bitter-almond oil, whereby that acid is resolved into ammonia and formic acid. Formobenzoic acid forms white crystals soluble in water. It is resolved by oxidizing agents into bitter-almond oil (C_7H_6O), and carbon dioxide.

Anisic Acid, $C_8H_8O_3$, or Methyl-paraoxybenzoic acid. $C_7H_5(CH_3)O_3$. — This acid is produced by oxidation of anisic aldehyde, $C_8H_8O_2$, in contact with platinum black, or by treatment with dilute nitric acid (strong nitric acid would convert it into nitranisic acid); also by dropping anisic aldehyde into fused potash:

$$C_8H_8O_2 + KOH = C_8H_7KO_3 + H_2.$$

It is usually prepared by oxidizing anise-camphor, $C_{10}H_{12}O$, or the crude oils of anise, fennel, and tarragon, which contain that compound in solution, with nitric acid. Anisic aldehyde is first produced, according to the equation:

$$\underset{\text{Anise-camphor.}}{C_{10}H_{12}O} + O_6 = \underset{\text{Anisic aldehyde.}}{C_8H_8O_2} + \underset{\text{Oxalic acid.}}{C_2H_2O_4} + OH_2,$$

and subsequently oxidized to anisic acid. It may also be produced synthetically by treating potassium para-oxybenzoate with methyl iodide, whereby the methylic ether of methyl-paraoxybenzoic acid is produced:

$$\underset{\text{Potassium para-oxybenzoate.}}{C_7H_4K_2O_3} + 2CH_3I = 2KI + \underset{\text{Methylic methyl-paraoxybenzoate.}}{C_7H_4(CH_3)O_3.CH_3}$$

* *Kolbe* and *Lautemann*, Ann. Ch. Pharm. cxv. 203.

And boiling this compound with potash:

$$\underset{\text{Methylic methyl-paraoxybenzoate.}}{C_7H_4(CH_3)O_3.CH_3} + OH_2 = \underset{\text{Methyl alcohol.}}{CH_3(OH)} + \underset{\text{Methyl-para-benzoic acid.}}{C_7H_5(CH_3)O_3}$$

Ethyl-parabenzoic acid, $C_7H_5(C_2H_5)O_3$, may be produced in a precisely similar manner.

Anisic acid crystallizes in brilliant colorless prisms melting at 175° C. (347° F.), moderately soluble in hot water, easily in alcohol and ether. It yields substitution-products with chlorine, bromine, and nitric acid. By distillation with lime or baryta it is resolved in carbon dioxide and anisol or methyl-phenol (p. 551):

$$C_8H_8O_3 = CO_2 + C_7H_8O_2.$$

Anisic acid is monobasic, and most of its salts are crystallizable.

Phloretic Acid, $C_9H_{10}O_3$, is produced, together with phloroglucin, by the action of potash on phloretin, a substance resulting from the action of dilute acids on phlorizin (p. 581):

$$\underset{\text{Phloretin.}}{C_{15}H_{14}O_5} + OH_2 = \underset{\text{Phloretic acid.}}{C_9H_{10}O_3} + \underset{\text{Phloroglucin.}}{C_6H_6O_3}$$

It forms prismatic crystals melting at about 129° C. (264° F.), somewhat less soluble in water than in alcohol; produces a green color with ferric chloride. When heated with lime or baryta, it is resolved into carbon dioxide and *phlorol*, $C_9H_{10}O$, which passes over as a brown oily distillate:

$$C_9H_{10}O_3 + BaO = CO_3Ba + C_8H_{10}O.$$

Phloretic acid is bibasic, forming acid and neutral salts.

Another acid containing $C_9H_{10}O_3$ is formed by the action of potash on the cyano-hydrate or cyanhydrin of anisic alcohol, $C_8H_{10}O_2$:

$$\underset{\text{Anisic cyanhydrin.}}{C_8H_8(CN)(OH)} + 2OH_2 = NH_3 + \underset{\text{Acid.}}{C_9H_{10}O_3}$$

Thymotic and **Thymyl-carbonic Acids**, $C_{11}H_{14}O_3$. — These isomeric acids are produced simultaneously by the action of sodium and carbon dioxide on thymol, $C_{10}H_{14}O$ (p. 554); and are separated in the same manner as the homologous compounds, cresyl-carbonic and cresotic acids. Thymotic acid is a crystalline body, melting at 120°, nearly insoluble in cold, slightly soluble in boiling water; it produces a fine blue color with ferric chloride. Heated with baryta, it is resolved into carbon dioxide and thymol.

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5. — Series $C_n H_{2n-10}O_3$.

Coumaric Acid, $C_9H_8O_3$, the only known acid of this series, is produced by the action of boiling potash solution on coumarin, $C_9H_6O_2$, the odoriferous principle of the Tonka bean. It crystallizes in laminæ, having a bitter taste, soluble in water, alcohol, and ether, melting at 190° C. (374° F.). Fused with potash, it gives off hydrogen, and yields potassium salicylate and apparently also acetate:

$$C_9H_8O_3 + 2KOH = C_7H_5KO_3 + C_2H_3KO_2 + H_2.$$

It is monobasic, and decomposes carbonates.

There are no known acids belonging to the series $C_nH_{2n-12}O_3$ and $C_nH_{2n-14}O_3$.

6. — Series $C_nH_{2n-16}O_3$.

Benzilic Acid, $C_{14}H_{12}O_3$. — This acid is produced by the action of alcoholic potash on benzoin, $C_{14}H_{12}O_2$, a polymeric modification of benzoic aldehyde, $C_7H_6O_2$, which remains in the retort when the crude oil is distilled with lime or iron-oxide to free it from hydrocyanic acid; or on benzile, $C_{14}H_{10}O_2$, a crystalline substance formed from benzoin by the action of chlorine. On saturating the alkaline solution with hydrochloric acid, and leaving the filtered liquid to cool, benzilic acid separates in small colorless transparent crystals, slightly soluble in cold, more soluble in boiling water; it melts at 120° C. (248° F.), and cannot be volatilized without decomposition. It dissolves in cold strong sulphuric acid with fine carmine color.

DIATOMIC AND BIBASIC ACIDS.

These acids contain the group oxatyl, CO_2H, twice, and must therefore contain four atoms of oxygen. They may all be included in the general formula, $R''(CO_2H)_2$,—R denoting a diatomic hydrocarbon-radical, — or they may be regarded as compounds of oxygenated radicals with two equivalents of hydroxyl, *e. g.*, succinic acid $= (C_4H_4O_2)''(OH)_2$.

They are produced: — 1. By oxidation of the corresponding glycols, $R''(CH_2OH)_2$, the change consisting in the substitution of O_2 for H_4 (p. 557). In this manner oxalic acid, $C_2H_2O_4$, is formed from ethene alcohol, $C_2H_6O_2$, and malonic acid, $C_3H_4O_4$, from propene alcohol, $C_3H_8O_2$; but the higher glycols split up under the influence of oxidizing agents, and do not yield bibasic acids containing the same number of carbon-atoms as themselves.

2. By boiling the cyanides of diatomic alcohol-radicals with alcoholic potash; *e. g.*:

$$\underset{\text{Propene cyanide.}}{(C_3H_6)''(CN)_2} + 2KOH + 2OH_2 = 2NH_3 + \underset{\text{Potassium pyrotartrate.}}{(C_3H_6)''(CO_2K)_2}$$

This reaction is analogous to that by which the fatty acids are formed from the cyanides of the monatomic alcohol-radicals, C_nH_{2n+1} (p. 599).

3. By the addition of hydrogen to other acids containing a smaller proportion of that element; in this manner succinic acid, $C_4H_6O_4$, is formed from fumaric acid, $C_4H_4O_4$.

4. By the action of heat on acids of more complicated structure; *e. g.*:

$$\underset{\text{Tartaric acid.}}{2C_4H_6O_6} = 3CO_2 + 2OH_2 + \underset{\text{Pyrotartaric acid.}}{C_5H_8O_4}$$

5. Many of these acids are produced by the action of powerful oxidizers on a variety of organic bodies: thus, succinic acid, $C_4H_6O_4$, and its homologues, are produced by treating various fatty and resinous bodies with nitric acid.

The known acids of this group belong to the series $C_nH_{2n-2}O_4$, $C_nH_{2n-4}O_4$, $C_nH_{2n-8}O_4$, and $C_nH_{2n-10}O_4$. The acids of the first series, and probably also those of the third and fourth, are saturated compounds; but those of the second are unsaturated, being capable of taking up two atoms of hydrogen, bromine, and other monad elements, whereby they are converted into acids of the first series.

1. — Oxalic or Succinic Series, $C^nH_{2n-2}O_4$.

The known acids of this series are:

Oxalic acid . .	$C_2H_2O_4$	Pimelic acid . .	$C_7H_{12}O_4$
Malonic acid . .	$C_3H_4O_4$	Suberic acid . .	$C_8H_{14}O_4$
Succinic acid . .	$C_4H_6O_4$	Anchoic acid . .	$C_9H_{16}O_4$
Pyrotartaric acid .	$C_5H_8O_4$	Sebic acid . .	$C_{10}H_{18}O_4$
Adipic acid . .	$C_6H_{10}O_4$	Roccellic acid .	$C_{17}H_{32}O_4$

Oxalic Acid, $C_2H_2O_4 = \begin{matrix}COOH\\|\\COOH\end{matrix} = (C_2O_2)''(OH)_2$. — This important acid exists ready formed in many plants as a potassium or calcium-salt, and is produced by the oxidation of a great variety of organic compounds. In some cases the reaction consists in a definite substitution of oxygen for hydrogen; thus oxalic acid is formed from ethene alcohol, $C_2H_6O_2$, by substitution of O_2 for H_4, and from ethyl alcohol, C_2H_6O, by the same substitution and further addition of one atom of oxygen. But in most cases the reaction is more complex, consisting in a complete breaking up of the molecule. In this manner oxalic acid is produced in great abundance from more highly carbonized organic substances, such as sugar, starch, cellulose, &c., by the action of nitric acid, or by fusion with caustic alkalies.

Oxalic acid is also produced: *a*. As a sodium or potassium-salt by direct combination of the alkali-metal with carbon dioxide:

$$2CO_2 + Na_2 = C_2O_4Na_2.$$

The sodium-salt is obtained by passing the carbon dioxide over a heated mixture of sodium and sand; the potassium-salt, by heating potassium amalgam in the gas.*

β. As an ammonium-salt, together with other products, in the decomposition of cyanogen by water:

$$C_2N_2 + 4OH_2 = C_2(NH_4)_2O_4.$$

γ. As a potassium-salt by heating potassium formate with excess of potash:

$$2CHKO_2 = C_2K_2O_4 + H_2.$$

Preparation.—1. By the oxidation of sugar with nitric acid:

$$C_{12}H_{22}O_{11} + O_{18} = 6C_2H_2O_4 + 5OH_2.$$

One part of sugar is gently heated in a retort with 5 parts of nitric acid of sp. gr. 1·42, diluted with twice its weight of water; copious red fumes are then disengaged, and the oxidation of the sugar proceeds with violence and rapidity. When the action slackens, heat may be again applied to the vessel, and the liquid concentrated, by distilling off the superfluous nitric acid, until it deposits crystals on cooling. These are drained, redissolved in a small quantity of hot water, and the solution is set aside to cool.

2. By heating sawdust with caustic alkali.

Many years ago, Gay-Lussac observed that wood and several other organic substances were converted into oxalic acid by fusion with caustic potash. Messrs. Roberts, Dale & Co. have lately founded upon this observation a new method for the preparation of oxalic acid, which furnishes this acid much cheaper than any other process. A mixed solution of the hydrates of sodium and potassium in the proportion of two equivalents of the former to one of the latter, is evaporated to about 1·35 sp. gr. and then mixed with sawdust, so as to form a thick paste, which is placed in thin

* *Kolbe* and *Drechsel*, Chem. Soc. Journal [2], vi. 121.

layers on iron plates. The mixture is now gradually heated, care being taken to keep it constantly stirred. The action of heat expels a quantity of water, and the mass intumesces strongly, with disengagement of much inflammable gas, consisting of hydrogen and carbonetted hydrogen. The mixture is now kept for some hours at a temperature of 204° C. (400° F.), care being taken to avoid charring, which would cause a loss of oxalic acid. The product thus obtained is a gray powder; it is now treated with water at about 15·5° C. (60° F.), which leaves the sodium oxalate undissolved. The supernatant liquid is drawn off, evaporated to dryness, and heated in furnaces to recover the alkalies, which are caustified and used for a new operation. The sodium oxalate is washed and decomposed by boiling with slaked lime, and the resulting calcium oxalate is again decomposed by means of sulphuric acid. The liquid decanted from the calcium sulphate is evaporated to crystallization in leaden vessels, and the crystals are purified by re-crystallization.

Oxalic acid separates from a hot solution in colorless, transparent crystals derived from an oblique rhombic prism, and consisting of $C_2H_2O_4 . 2OH_2$. The two molecules of crystallization-water may be expelled by a very gentle heat, the crystals crumbling down to a soft white powder, consisting of anhydrous oxalic acid, $C_2H_2O_4$, which may be sublimed in great measure without decomposition. The crystallized acid, on the contrary, is decomposed by a high temperature into formic acid, carbon monoxide and carbon dioxide, without leaving any solid residue:

$$2C_2H_2O_4 = CH_2O_2 + CO + 2CO_2 + OH_2.$$

The crystals of oxalic acid dissolve in 8 parts of water at 15·5°, and in their own weight, or less, of hot water: they are also soluble in spirit. The aqueous solution has an intensely sour taste and most powerful acid reaction, and is highly poisonous. The proper antidote is chalk or magnesia. Oxalic acid is decomposed by hot oil of vitriol into a mixture of carbon monoxide and carbon dioxide: it is slowly converted into carbonic acid by nitric acid, whence arises a considerable loss in the process of manufacture from sugar. The dioxides of lead and manganese effect the same change, becoming reduced to monoxides, which form salts with the unaltered acid.

Oxalates.—Oxalic acid, like other bibasic acids, forms with monatomic metals, neutral or normal salts containing $C_2M_2O_4$, and acid salts, C_2HMO_4. With potassium and ammonium it likewise forms hyper-acid salts, *e. g.*, $C_2HKO_4 . C_2H_2O_4$, or $C_4H_3KO_8$. With most diatomic metals it forms only neutral salts, $C_2M''O_4$; with barium and strontium, however, it forms acid salts analogous to the hyper-acid oxalates of the alkali-metals. It also forms numerous well-crystallized double salts. It is one of the strongest acids, decomposing dry sodium chloride when heated, with evolution of hydrochloric acid, and converting sodium chloride or nitrate in aqueous solution into acid oxalate.

The oxalates of the alkali-metals are soluble in water: the rest are for the most part insoluble in water, but soluble in dilute acids.

All oxalates are decomposed by heat. The oxalates of the alkali-metals, and also of the alkaline earth-metals, if not too strongly heated, give off carbon monoxide and leave carbonates, while the oxalates of those metals whose carbonates are decomposed by heat (zinc and magnesium, for example) give off carbon monoxide and carbon dioxide, and leave metallic oxides. The oxalates of the more easily reducible metals (silver, copper, &c.) give off carbon dioxide and leave the metal; the lead-salt leaves suboxide of lead, and gives off 3 volumes of carbon dioxide to 1 volume of carbon monoxide:

$$2C_2Pb_4O_4 = Pb_2O + 3CO_2 + CO.$$

Oxalates heated with *sulphuric acid* give off carbon monoxide and dioxide, and leave a residue of sulphate. In this case, as well as in the decomposition by heat alone, no separation of carbon takes place, and consequently the residue does not blacken: this character distinguishes the oxalates from the salts of all other carbon acids.

Oxalic acid and the soluble oxalates give with *calcium chloride* a precipitate of calcium oxalate, insoluble in water and in acetic acid, but soluble in hydrochloric and nitric acid. This reaction affords a very delicate test for the presence of oxalic acid: the insolubility of the precipitated oxalate in acetic acid distinguishes it at once from the phosphate.

Potassium Oxalates.—The *neutral salt*, $C_2K_2O_4 . 2$ Aq., prepared by neutralizing oxalic acid with potassium carbonate, crystallizes in transparent rhombic prisms, which become opaque and anhydrous by heat, and dissolve in 3 parts of water.—The *acid oxalate* or *binoxalate*, $C_2HKO_4 . 2$ Aq., sometimes called *salt of sorrel*, from its occurrence in that plant, is found also in other species of *Rumex*, in *Oxalis acetosella*, and in garden rhubarb, associated with malic acid. It is easily prepared by dividing a solution of oxalic acid in hot water into two equal portions, neutralizing one with potassium carbonate, and adding the other: the salt crystallizes, on cooling, in colorless rhombic prisms. The crystals have a sour taste, and require 40 parts of cold, and 6 of boiling water for solution. A solution of this salt is often used for removing ink from paper. The *hyper-acid oxalate* or *quadroxalate*, $C_2HKO_4 . C_2H_2O_4 . 2$ Aq., is prepared by a process similar in principle to that last described. The crystals are modified octohedrons, and are less soluble than those of the binoxalate, which the salt in other respects resembles.

Sodium oxalate, $C_2Na_2O_4$, has but little solubility; a *binoxalate* exists.

Ammonium Oxalates.—The *neutral salt*, $C_2(NH_4)_2O_4 . 2$ Aq., is prepared by neutralizing a hot solution of oxalic acid with ammonium carbonate. It crystallizes in long, colorless, rhombic prisms, which effloresce in dry air from loss of water of crystallization. They are not very soluble in cold water, but dissolve freely by the aid of heat.

The dry salt when heated in a retort gives off water, and yields a sublimate of *oxamide*:*

$$\underset{\text{Ammonium oxalate.}}{(C_2O_2)''(ONH_4)_2} = 2OH_2 + \underset{\text{Oxamide.}}{(C_2O_2)''(NH_2)_2}.$$

When distilled with phosphoric oxide, it gives up four molecules of water and yields a considerable quantity of *cyanogen*, $C_2(NH_4)_2O_4 - 4OH_2 = 2CN$. Other products are, however, formed at the same time.

Acid ammonium oxalate, or *binoxalate*, $C_2H(NH_4)O_4 . Aq.$, is still less soluble than the neutral salt. When heated in an oil-bath to 232° C. (450° F.), it loses one molecule of water, and yields *oxamic acid*, $C_2H_3NO_3$, or $(C_2O_2)''(OH)(NH_2)$; other products are, however, formed at the same time.

Calcium Oxalate, $C_2Ca''O_4 . 4$ Aq., is formed whenever oxalic acid or an oxalate is added to a soluble calcium-salt; it falls as a white powder, which acquires density by boiling, and is but little soluble in dilute hydrochloric, and quite insoluble in acetic acid. Nitric acid dissolves it easily. When dried at 100°, it retains a molecule of water, which may be driven off by a rather higher temperature. Exposed to a red heat in a close vessel, it is converted into calcium carbonate, with escape of carbon monoxide.

The oxalates of *barium*, *zinc*, *manganese*, *copper*, *nickel*, *cobalt*, and *ferrous oxalate*, are nearly insoluble in water: *magnesium oxalate* is sparingly soluble; *ferric oxalate* is freely soluble.—*Potassio-chromic oxalate*, $(C_2O_4)_3Cr'''$

* See the chapter on Amides.

$K_2 . 3$ Aq., prepared by dissolving in hot water 1 part of potassium bichromate, 2 parts of potassium binoxalate, and 2 parts of crystallized oxalic acid, is one of the most beautiful salts known. The crystals appear black by reflected light from the intensity of their color, which is pure deep blue: they are very soluble. A corresponding *potassio-ferric oxalate* has been formed: it crystallizes freely, and has a beautiful green color.

Ethyl Oxalates.—The *neutral oxalate*, or *Oxalic ether*, $C_2O_4(C_2H_5)_2$, is most easily obtained by distilling together 4 parts of potassium binoxalate, 5 parts of oil of vitriol, and 4 parts of strong alcohol. The distillation may be pushed nearly to dryness, and the receiver kept warm to dissipate any ordinary ether that may be formed. The product is mixed with water, by which the oxalic ether is separated from the undecomposed spirit: it is repeatedly washed to remove adhering acid, and re-distilled in a small retort, the first portion being received apart and rejected. Another very simple process consists in digesting equal parts of alcohol and dehydrated oxalic acid in a flask furnished with a long glass tube in which the volatilized spirit may condense. After six or eight hours' digestion, the mixture generally contains only traces of unetherified oxalic acid.

Pure oxalic ether is a colorless, oily liquid, of pleasant aromatic odor, and 1·09 sp. gr. It boils at 183·8° C. (362° F.), is but little soluble in water, and is readily decomposed by caustic alkalies into a metallic oxalate and alcohol. With solution of ammonia in excess, it yields oxamide and alcohol; thus:

$$\underset{\text{Ethyl oxalate.}}{(C_2O_2)''(OC_2H_5)_2} + 2NH_3 = \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2HOC_2H_5} + \underset{\text{Oxamide.}}{(C_2O_2)''(NH_2)_2}$$

This is the best process for preparing oxamide.

When dry gaseous ammonia is conducted into a vessel containing oxalic ether, the gas is rapidly absorbed, and a white solid substance produced, which is soluble in hot alcohol, and separates on cooling in colorless, transparent, scaly crystals. They dissolve in water, and are both fusible and volatile. This substance is *oxamethane*, the ethylic ether of oxamic acid (p. 659):

$$\underset{\text{Ethyl oxalate.}}{(C_2O_2)''(OC_2H_5)_2} + NH_3 = \underset{\text{Alcohol.}}{HOC_2H_5} + \underset{\text{Ethyl oxamate.}}{C_2O_2(NH_2)(OC_2H_5)}$$

The same substance is formed when ammonia in small quantity is added to a solution of oxalic ether in alcohol.

When oxalic ether is treated with dry chlorine in excess in sunshine, a white, colorless, crystalline, fusible body is produced, insoluble in water, and instantly decomposed by alcohol. It consists of *perchlorethylic oxalate*, $C_6Cl_{10}O_4$, or $C_2O_4(C_2Cl_5)_2$, or oxalic ether in which the whole of the hydrogen is replaced by chlorine.

Ethyl oxalate is converted by potassium or sodium into ethyl carbonate, with evolution of carbon monoxide: $C_2(C_2H_5)_2O_4 = C(C_2H_5)_2O_3 + CO$; but the reaction is complicated by the formation of several other products.

When ethyl oxalate is agitated with sodium amalgam in a vessel externally cooled, a product is obtained which is separated by ether into a soluble and an insoluble portion, the latter consisting of fermentable sugar, together with sodium oxalate and at least one other sodium-salt, while the ethereal solution yields, by spontaneous evaporation, crystals having the composition $C_{11}H_{18}O_8$, and consisting of the ethylic ether of a tribasic acid, $C_5H_6O_8$, called *desoxalic acid*, because it is produced by deoxidation of oxalic acid: $5C_2H_2O_4 + 5H_2 = 2C_5H_6O_8 + 4OH_2$; and *racemo-carbonic acid*, because it contains the elements of racemic acid, $C_4H_6O_6$, and carbon dioxide, CO_2, and is resolved into those two compounds when its aqueous solution is

heated in a sealed tube with a small quantity of sulphuric acid. The decomposition of ethylic oxalate by sodium amalgam has not been completely investigated, but the formation of desoxalic acid and glucose may be represented by the equation:

$$\underset{\text{Oxalic acid.}}{8C_2H_2O_4} + 14H_2 = \underset{\text{Desoxalic acid.}}{2C_5H_6O_8} + \underset{\text{Glucose.}}{C_6H_{12}O_6} + 10H_2O.$$

Ethyl oxalate treated with zinc-ethyl, and afterward with water, yields the ethylic ether of diethoxalic acid, $C_2H_2(C_2H_5)_2O_8$, and similar products with zinc-methyl and zinc-amyl (p. 630).

Acid ethyl oxalate, or *Ethyloxalic acid*, $C_2H(C_2H_5)O_4$, or $(C_2O_2)''(OH)(OC_2H_5)$, is obtained as a potassium-salt by adding to a solution of neutral ethyl oxalate in absolute alcohol, a quantity of alcoholic potash less than sufficient to convert the whole into potassium oxalate and alcohol; on dissolving this salt in hydrated alcohol, carefully saturating with sulphuric acid, and neutralizing with carbonate of lead or barium, the ethyloxalate of lead or barium is obtained. — The acid itself is prepared by decomposing either of these salts with sulphuric acid; but it is very unstable, and is decomposed by concentration into alcohol and oxalic acid. — The *potassium-salt*, $C_2(C_2H_5)KO_4$, forms crystalline scales which begin to decompose toward 100°.

Methyl Oxalate, $C_2(CH_3)_2O_4$, or $(C_2O_2)''(OCH_3)_2$, is easily prepared by distilling a mixture of equal weights of oxalic acid, wood-spirit, and oil of vitriol. A spirituous liquid collects in the receiver, which, when exposed to the air, quickly evaporates, leaving the methyl oxalate in the form of rhombic, transparent, crystalline plates, which may be purified by pressure between folds of bibulous paper, and redistilled from a little oxide of lead. The product is colorless, and has the odor of ethyloxalate; it melts at 51° C. (123° F.), and boils at 161° C. (321° F.), dissolves freely in alcohol and wood-spirit, and also in water, which, however, rapidly decomposes it, especially when hot, into oxalic acid and wood-spirit. The alkaline hydrates effect the same change even more easily. Solution of ammonia converts it into oxamide and methyl alcohol. With dry ammoniacal gas it yields methyl oxamate, or oxamethylane, $(C_2O_2)''(NH_2)(OCH_3)$, a white, solid substance, which crystallizes from alcohol in pearly cubes.

Ethene Oxalate, $C_2(C_2H_4)''O_4$, or $(C_2O_2)''(C_2H_4O_2)''$, appears to be formed by the action of ethene bromide on silver oxalate.

Malonic Acid, $C_3H_4O_4 = (CH_2)''.(CO_2H)_2 = (C_3H_2O_2)''(OH)_2$. — This acid is formed by the slow oxidation of propene glycol (p. 595):

$$C_3H_6O_2 + O_4 = 2OH_2 + C_3H_4O_4;$$

also by oxidizing malic acid with a cold solution of potassium chromate:

$$\underset{\text{Malic acid.}}{C_4H_6O_5} + O_2 = CO_2 + OH_2 + \underset{\text{Malonic acid.}}{C_3H_4O_4};$$

and by the action of alkalies on cyanacetic acid, or, better, on ethyl cyanacetate:

$$\underset{\text{Ethyl cyanacetate.}}{C_2H_2(CN)O_2.C_2H_5} + 3OH_2 = NH_3 + \underset{\text{Alcohol.}}{C_2H_6O} + \underset{\text{Malonic acid.}}{C_3H_4O_4}$$

Malonic acid forms large rhombohedral crystals, soluble in water and alcohol, melting at 140° C. (284° F.), and resolved at 150° C. (302° F.) into carbon dioxide and acetic acid. — Its relations to bodies of the uric acid group will be noticed hereafter.

Succinic Acid, $C_4H_6O_4 = (C_2H_4)''(CO_2H)_2 = (C_4H_4O_2)''(OH)_2$. — This acid is produced: 1. By heating ethene cyanide * with alcoholic potash:

$$C_2H_4(CN)_2 + 4OH_2 = 2NH_3 + C_4H_6O_4.$$

2. By the action of nascent hydrogen (evolved by sodium-amalgam) on maleic acid, or its isomer, fumaric acid, $C_4H_4O_4 + H_2 = C_4H_6O_4$. — 3. By the action of hydriodic acid (or water and phosphorus iodide) on malic acid, $C_4H_6O_5$, or tartaric acid, $C_4H_6O_6$, the reaction consisting in the abstraction of 1 or 2 atoms of oxygen, with formation of water and separation of iodine. — 4. By the fermentation of malic or fumaric acid, and of many other organic substances, especially under the influence of putrefying casein; in small quantity also during the alcoholic fermentation of sugar (p. 516, foot-note). — 5. By the oxidation of many organic substances, especially of the fatty acids, $C_nH_{2n}O_2$, and their glycerides, under the influence of nitric acid. Its formation from butyric acid is represented by the equation $C_4H_8O_2 + O_3 = OH_2 + C_4H_6O_4$.

Succinic acid occurs ready formed in amber and in certain lignites, and occasionally in the animal organism. By heating amber in iron retorts, it may be obtained in colored crystals, which may be purified by treatment with nitric acid and re-crystallization from boiling water. The acid is, however, more advantageously prepared by the fermentation of malic acid, the crude calcium malate obtained by neutralizing the juice of mountain-ash berries with chalk or slaked lime being used for the purpose. This salt is mixed in an earthen jar with water and yeast, or decaying cheese, and left for a few days at 30° or 40°; the calcium succinate thus obtained is decomposed by dilute sulphuric acid; and the succinic acid is purified by crystallization from water and by sublimation.

Succinic acid crystallizes in colorless, oblique rhombic prisms, which dissolve in 5 parts of cold and in 3 parts of boiling water: it melts at 180° C. (356° F.) and boils at 235° C. (455° F.), at the same time undergoing decomposition into water and *succinic oxide*, or *anhydride*, $C_4H_4O_3$, or $(C_4H_4O_2)''O$. The same compound is formed by the action of phosphorus pentachloride on succinic acid: $C_4H_6O_4 + PCl_5 = 2HCl + POCl_3 + C_4H_4O_3$. It is a white mass, less soluble in water, but more soluble in alcohol, than succinic acid.

Succinic acid, being bibasic, forms, with monad metals, acid and neutral salts, $C_4H_5MO_4$ and $C_4H_4M_2O_4$, and with dyad metals, neutral salts, containing $C_4H_4M''O_4$, and acid salts, $C_4H_4MO_4 . C_4H_6O_4$. — There are also a few double succinates, several basic lead-salts, and a hyperacid potassium-salt.

Succinic acid is distinguished from benzoic acid by not being precipitated from its soluble salts by mineral acids, and by forming a white precipitate with barium chloride, on addition of ammonia and alcohol.

Pyrotartaric Acid, $C_5H_8O_4 = (C_3H_6)''(CO_2H)_2 = (C_5H_6O_2)''(OH)_2$, is produced by the dry distillation of tartaric acid, and by the action of alcoholic potash on propene cyanide, $C_3H_6(CN)_2$. It forms rhombic prisms, very soluble in water, alcohol, and ether; melts at 112° C. (233° F.), volatilizes at about 200° C. (392° F.), being partly resolved into water and *pyrotartaric oxide*, $C_5H_6O_3$. It forms acid and neutral salts analogous to the succinates.

Adipic Acid, $C_6H_{10}O_4$, and **Pimelic Acid,** $C_7H_{12}O_4$, are produced by the oxidation of fats with nitric acid.

Suberic Acid, $C_8H_{14}O_4$, has long been known as a product of the oxida-

* Ethene cyanide is obtained by heating ethene bromide, $C_2H_4Br_2$, with an alcoholic solution of potassium cyanide.

tion of cork by nitric acid. Recently it has been produced, together with other acids of the series, by the long-continued action of nitric acid upon stearic and oleic acids and other fatty bodies. Suberic acid is a white crystalline powder, sparingly soluble in cold water, fusible and volatile by heat.

Anchoic Acid, or Lepargylic Acid, $C_9H_{16}O_4$, is formed, together with other products, by the action of nitric acid on Chinese wax and on the fatty acids of cocoa-nut oil. — *Azelaic acid*, obtained by oxidizing castor-oil with nitric acid, has the same composition as anchoic acid, but differs so much from it in physical properties, that it must be regarded as an isomeric or allotropic modification.

Sebic or Sebacic Acid, $C_{10}H_{18}O_4$, is a constant product of the destructive distillation of oleic acid, olein, and all fatty substances containing those bodies; it is extracted by boiling the distilled matter with water: it is also formed by the action of potash on castor-oil (see p. 652.) It forms small pearly crystals resembling those of benzoic acid. It has a faintly acid taste, is but little soluble in cold water, melts when heated, and sublimes unchanged.

Roccellic Acid, $C_{17}H_{32}O_4$, exists in *Roccella tinctoria*, and other lichens of the same genus, also in *Lecanora tartarea*, and is obtained by exhausting the first-mentioned plant with aqueous ammonia, precipitating the filtered liquor with calcium chloride, and decomposing the resulting calcium-salt with hydrochloric acid. When purified by solution in ether, it forms white, rectangular, four-sided tabular crystals, melting at 132° C. (270° F.), and subliming at 200° C. (392° F.), being partially converted at the same time into an oxide, $C_{17}H_{30}O_3$. This acid decomposes carbonates.

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2. — Fumaric Series $C^nH_{2n-4}O_4$.

This series includes the two following groups of isomeric acids:

Fumaric and Maleic acids	$C_4H_4O_4$
Itaconic, Citraconic, and Mesaconic acids .	$C_5H_6O_4$.

They are unsaturated compounds, capable of taking up two atoms of hydrogen, bromine, and other monad elements, and passing into acids of the preceding series.

Fumaric and Maleic Acids, $C_4H_4O_4 = (C_2H_2)''(CO_2H)_2 = (C_4H_2O_2)''(OH)_2$. When malic acid is heated in a small retort, nearly filled, it melts, emits water, and enters into ebullition, and a volatile acid passes over, which dissolves in the water of the receiver. After a time, small solid, crystalline scales make their appearance in the boiling liquid, and increase in quantity until the whole becomes solid. The process may now be interrupted, and the contents of the retort, after cooling, treated with cold water: unaltered malic acid is thereby dissolved out, and a less soluble acid is left behind, called *fumaric* acid, from its identity with an acid extracted from the common fumitory (*Fumaria officinalis*).

Fumaric acid forms small, white crystalline laminæ, which dissolve freely in hot water and alcohol, but require for solution about 200 parts of cold water: it is unchanged by hot nitric acid. When heated in a current of air it sublimes, but in a retort undergoes decomposition; this is a phenomenon often observed in organic bodies of small volatility. Fumaric acid forms acid and neutral metallic salts, and an ether, which, by the action of

ammonia, yields fumaramide, $(C_4H_2O_2)''(NH_2)_2$, in the form of a white, amorphous, insoluble powder.

The volatile acid produced simultaneously with fumaric acid is called *maleic acid;* it may be obtained in crystals by evaporation in a warm place. It is very soluble in water, alcohol, and ether, has a strongly acid taste and reaction, and is convertible by heat into fumaric acid. Maleic and fumaric acids are formed from malic acid by separation of a molecule of water. Fumaric acid, when heated with bromine, combines with 2 atoms of that element, forming *dibromosuccinic acid*, $C_4H_4Br_2O_4$, which resembles in all its properties the dibrominated acid prepared from succinic acid by direct substitution. On heating fumaric acid with hydriodic acid, it passes into succinic acid. The same reaction takes place on treating fumaric acid with water and sodium-amalgam, $C_4H_4O_4 + H_2 = C_4H_6O_4$. The deportment of maleic acid with bromine and nascent hydrogen, is perfectly analogous to that of fumaric acid: when treated with hydriodic acid, it passes first into fumaric acid, and then into succinic acid (Kekulé).

Itaconic, Citraconic, and **Mesaconic Acids,** $C_5H_6O_4$. — The first two of these acids are produced by the action of heat on citric acid. When crystallized citric acid is heated in a retort it first melts in its water of crystallization, and then boils, giving off water. Afterwards, at about 175° C. (347° F.), vapors of acetone distil over, and a copious disengagement of carbon monoxide takes place. At this time the residue in the retort consists of aconitic acid. If the distillation be still continued, carbon dioxide is given off, and itaconic acid crystallizes in the neck of the retort. If these crystals be repeatedly distilled, an oily mass of citraconic oxide or anhydride is obtained, which no longer solidifies. These compositions are represented by the following equations:

$$\underset{\text{Citric acid.}}{C_6H_8O_7} - OH_2 = \underset{\text{Aconitic acid.}}{C_6H_6O_6}; \qquad \underset{\text{Aconitic acid.}}{C_6H_6O_6} - CO_2 = \underset{\text{Itaconic acid.}}{C_5H_6O_4};$$

$$\underset{\text{Itaconic acid.}}{C_5H_6O_4} - OH_2 = \underset{\text{Citraconic oxide.}}{C_5H_4O_3}$$

The citraconic oxide when exposed to the air absorbs moisture, and is converted into crystallized citraconic acid, $C_5H_6O_4$.

Mesaconic acid is produced by boiling itaconic acid with weak nitric acid. These three isomeric acids are all converted by nascent hydrogen into *pyrotartaric acid*, $C_5H_8O_4$. They also take up a molecule of hydrobromic acid, HBr, forming monobromopyrotartaric acid, $C_5H_7BrO_4$, or of bromine, Br_2, forming dibromopyrotartaric acid. Itaconic and citraconic acids are, however, more inclined to these transformations than mesaconic acid, which is altogether a more stable compound.*

Camphoric Acid, $C_{10}H_{16}O_4$, produced by heating camphor $(C_{10}H_{16}O)$ with nitric acid, is likewise included in the general formula, $C_nH_{2n-4}O_4$; but it appears to be a saturated compound, inasmuch as its ethylic ether shows no tendency to take up chlorine or other elements. The acid forms small colorless needles or plates, of acid and bitter taste, sparingly soluble in cold water. It melts when heated, and yields by distillation a colorless, crystalline, neutral substance, consisting of *camphoric oxide*, or *anhydride*, $C_{10}H_{14}O_3$. Calcium camphorate when distilled yields a volatile oil consisting of *phorone*, $C_9H_{14}O$, the ketone of camphoric acid:

$$C_{10}H_{14}CaO_4 = CO_3Ca + C_9H_{14}O.$$

* For an explanation of the isomerism between these three acids, see *Kekulé* (Bulletin de la Société Royale de Belgique [2], xxxiv. 8; also Laboratory, p. 369).

3.— Series $C_nH_{2n-6}O_4$.

The only known acid belonging to this series is:

Mellitic Acid, $C_4H_2O_4$, which occurs as an aluminium-salt in a very rare mineral called *mellite* or *honeystone*, found in deposits of lignite. It is soluble in water and alcohol, and is crystallizable, forming colorless needles. It is a bibasic acid, forming acid and neutral salts: the mellitates of the alkali-metals are soluble and crystallizable; those of the earths and heavy metals are mostly insoluble.

Ammonium mellitate yields by distillation *paramide* and *euchroic acid*. The former is a white, amorphous, insoluble substance, containing C_4HNO_2 (*i. e.*, acid ammonium mellitate, $C_4H(NH_4)O_4$ *minus* $2OH_2$), and convertible by boiling with water into acid ammonium mellitate. *Euchroic acid* forms colorless, sparingly soluble crystals, containing in the anhydrous state $C_6H_4N_2O_4$. In contact with metallic zinc and deoxidizing agents in general, it yields a deep blue insoluble substance called *euchrone*.

4.— Series $C_nH_{2n-8}O_4$.

Quinonic or *Quinoylic acid*, $C_6H_4O_4$, is not actually known, but its dichlorinated derivative, $C_6H_2Cl_2O_4$, is produced by the action of potash on tetrachloroquinone, $C_6Cl_4O_2$. It is a crystalline substance, which gives off water when heated. It is bibasic, forming acid and neutral salts.

Orsellinic acid, $C_8H_8O_4$, and *Evernic acid*, $C_9H_{10}O_4$, perhaps belong to the same series. They will be further noticed in the chapter on Coloring Matters.

5.— Series $C_nH_{2n-10}O_4$.

This series includes the isomeric acids, phthalic and terephthalic, $C_8H_6O_4$; also insolinic acid, $C_9H_8O_4$.

Phthalic Acid, $C_8H_6O_4$, also called *Alizaric* and *Naphthalic acid*, is produced by the action of nitric acid on naphthalene, dichloride of naphthalene, alizarin, and purpurin (the coloring matters of madder):

$C_{10}H_8$ Naphthalene.	+	O_8	=	$C_8H_6O_4$ Phthalic acid.	+	$C_2H_2O_4$ Oxalic acid.
$C_{10}H_6O_3$ Alizarin.	+	OH_2+O_4	=	$C_8H_6O_4$	+	$C_2H_2O_4$.
$2C_9H_6O_3$ Purpurin.	+	OH_2+O_5	=	$2C_8H_6O_4$	+	$C_2H_2O_4$.

It is usually prepared by treating naphthalene dichloride with boiling nitric acid.

Phthalic acid crystallizes in colorless plates: it is but slightly soluble in cold water, but dissolves freely in alcohol and ether. It is bibasic, forming acid and neutral salts. When heated, it loses a molecule of water, and leaves *phthalic oxide*, $C_8H_4O_3$. Treated with fuming nitric acid, it yields *nitro-phthalic acid*, $C_8H_5(NO_2)O_4$. When distilled with baryta, it gives off benzene:

$$C_8H_6O_4 + 2BaO = 2CO_3Ba + C_6H_6.$$

Terephthalic Acid, $C_8H_6O_4$, is produced by the oxidizing action of nitric acid on turpentine oil, lemon-oil, and other terpenes, also on cymene. It is a white, tasteless, crystalline powder, not perceptibly soluble in water, alcohol, or ether. It is distinguished from phthalic acid by subliming without alteration when heated, and not being resolved into water and an anhydride. Although bibasic, it forms no double salts, and shows but little tendency to form acid salts. Nearly all the terephthalates are soluble and crystallizable, and so inflammable that they may be set on fire by a spark from a flint and steel, and burn away slowly like tinder, emitting the odor of benzene.

Insolinic Acid, $C_9H_8O_4$, is produced by the action of potassium bichromate and sulphuric acid on cumic acid,* and by that of nitric acid on coal-tar cumene (trimethyl-benzene, p. 498), zylic acid being first produced, and afterward further oxidized to insolinic acid:†

$$\underset{\text{Cumic acid.}}{C_{10}H_{12}O_2} + O_6 = CO_2 + 2OH_2 + \underset{\text{Isolinic acid.}}{C_9H_8O_4}$$

$$\underset{\text{Cumene.}}{C_9H_{12}} + O_3 = \underset{\text{Zylic acid.}}{C_9H_{10}O_2} + OH_2$$

$$\underset{\text{Zylic acid.}}{C_9H_{10}O_2} + O_3 = \underset{\text{Insolinic acid.}}{C_9H_8O_4} + OH_2.$$

Insolinic acid is a white crystalline powder, and resembles terephthalic acid in being nearly insoluble in cold and sparingly soluble in hot water; from hot alcohol it separates in crystalline crusts. When heated it sublimes without previous fusion, and in part without decomposition. It is bibasic, forming neutral acid and double salts, also a neutral and acid ethylic ether (Hofmann).

TRIATOMIC AND MONOBASIC ACIDS.

These acids are derived from triatomic alcohols by substitution of O for H_2, as glyceric acid, $C_3H_6O_4$, from glycerin, $C_3H_8O_3$:

CH_2OH	CH_2OH
$\vert$	$\vert$
$CHOH$	$CHOH$
$\vert$	$\vert$
CH_2OH	$COOH$
Glycerin.	Glyceric acid.

The known acids of the group are:

Glyoxylic acid .	$C_2H_4O_4$	Eugetic acid .	$C_{11}H_{12}O_4$
Glyceric acid . .	$C_3H_6O_4$	Piperic acid . .	$C_{12}H_{10}O_4$
Oxysalicylic acid .	$C_7H_6O_4$		

Glyoxylic Acid, $C_2H_4O_4 = \begin{matrix} OH \\ \vert \\ CHOH. \\ \vert \\ COOH \end{matrix}$ — This acid is produced: 1. By the action of nascent hydrogen (evolved by zinc and sulphuric acid) on oxalic acid: $C_2H_2O_4 + H_2 = C_2H_4O_4$.

* *Hofmann*, Ann. Ch. Pharm. xcvii. 197.
† *Hirzel* and *Beilstein*, Bull. Soc. Chim. de Paris [2], vii. 345.

2. By boiling silver bromoglycollate with water:

$$C_2H_2AgBrO_3 + OH_2 = AgBr + C_2H_4O_4.$$

3. By the oxidation of glycol, alcohol, or glyoxal with nitric acid:

$$\underset{\text{Glycol.}}{C_2H_6O_2} + O_3 = C_2H_4O_4 + OH_2$$

$$\underset{\text{Alcohol.}}{C_2H_6O} + O_4 = C_2H_4O_4 + OH_2$$

$$\underset{\text{Glyoxal.}}{C_2H_2O_2} + O + OH_2 = C_2H_4O_4.$$

Glyoxylic acid may be obtained by evaporation in the form of a viscid transparent syrup, which dissolves readily in water, and distils without alteration at 100°. It dissolves zinc without evolution of hydrogen, and is converted into glycolic acid: $C_2H_4O_4 + H_2 = C_2H_4O_3 + OH_2$. Glyoxylic acid forms salts most of which are represented by the formulæ $C_2H_3O_4M$, and $(C_2H_3O_4)_2M''$, *e. g.*, the *silver-salt* is $C_2H_3O_4Ag$, and the *calcium-salt*, $(C_2H_3O_4)_2Ca''$. The *ammonium-salt*, however, has the composition $C_2HO_2(NH_4)$, apparently derived from an acid containing $C_2H_2O_3$. This is indeed the formula originally assigned to glyoxylic acid by Debus,* who discovered it. This formula is perfectly consistent with the formation of the acid by oxidation of glyoxal, glycol, and alcohol; but, on the other hand, its formation from oxalic and from bromoglycolic acid seems rather to show that it consists of $C_2H_4O_4$.† Moreover, if the acid were really $C_2H_2O_3$, it would be necessary to suppose that all the glyoxylates, except the ammonium salt, contain water of crystallization, the silver-salt, for example, being $C_2HO_3Ag.OH_2$; now, there is no other known instance of a silver-salt containing water. The ammonium-salt above mentioned is probably an amide, $(C_2H_3O_3)NH_2$, formed from the true ammonium glyoxylate, $C_2H_3O_4(NH_4)$, by abstraction of water.

Glyceric Acid, $C_3H_6O_4$. — This acid, isomeric with pyruvic acid, is produced by the action of nitric acid on glycerin: also by the spontaneous decomposition of nitroglycerin, and by heating glycerin with bromine and a large quantity of water to 100° in a sealed tube:

$$C_3H_8O_3 + 2Br_2 + OH_2 = 4HBr + C_3H_6O_4.$$

Glyceric acid, when concentrated, is a colorless non-crystallizing syrup which, when heated for some time to 105° C. (221° F.), gives off water and is converted into glyceric oxide or anhydride, $C_3H_4O_3$. This acid, treated with phosphorus iodide, is converted into iodopropionic acid, $C_3H_5IO_2$.

The glycerates, $C_3H_5O_4M'$ and $(C_3H_5O_4)_2M''$, are soluble in water and crystallize well. They are not reddened by ferrous sulphate, and are thereby distinguished from the pyruvates, with which they are isomeric.

Oxysalicylic Acid, $C_7H_6O_4$, is produced by boiling a solution of iodosalicylic acid, $C_7H_5IO_3$, with potash. It forms highly lustrous needles, soluble in water, alcohol, and ether. The aqueous solution is colored deep blue by ferric chloride. The crystallized acid melts at 193° C. (379° F.), and is resolved between 210° and 212° C. (410°–414° F.) into carbonic dioxide and oxyphenol or pyrocatechin, $C_6H_6O_2$ (p. 562), and its isomer, hydro-quinone. The oxysalicylates are very unstable.

There are three acids isomeric with oxysalicylic acid, viz., *hypogallic acid*, produced by the action of boiling hydriodic acid on hemipinic acid, $C_{10}H_{10}O_6$:

$$C_{10}H_{10}O_6 + 2HI = C_7H_6O_4 + 2CH_3I + CO_2;$$

* Phil. Mag. [4], xii. 36.

† *Perkin* and *Duppa*, Chem. Soc. J. [2], vi. 197.

protocatechuic acid, produced, together with oxalic and acetic acids, by the action of melted potash on piperic acid, $C_{12}H_{10}O_4$:

$$C_{12}H_{10}O_4 + 8OH_2 = C_7H_6O_4 + C_2H_2O_4 + C_2H_4O_2 + CO_2 + 7H_2,$$

and *carbohydroquinonic acid*, produced by a peculiar transformation of quinic acid.

Eugetic Acid, $C_{11}H_{12}O_4$, is produced by the action of carbon dioxide and sodium on eugenol or eugenic acid (oxidized essence of cloves):

$$\underset{\text{Sodium eugenate.}}{C_{10}H_{11}NaO_2} + CO_2 = \underset{\text{Sodium eugetate.}}{C_{11}H_{11}NaO_4}$$

It crystallizes from hot aqueous solution in long colorless prisms, melting at 124° C. (255° F.), slightly soluble in cold water, very soluble in alcohol and ether. The aqueous solution is colored blue by ferric chloride. The acid is resolved by heat into carbon dioxide and eugenic acid.

Piperic Acid, $C_{12}H_{10}O_4$, is produced, together with piperidine, by boiling piperine (an alkaloïd from pepper) with potash:

$$\underset{\text{Piperine.}}{C_{17}H_{19}NO_3} + OH_2 = \underset{\text{Piperic acid.}}{C_{12}H_{10}O_4} + \underset{\text{Piperidine.}}{C_5H_{11}N}$$

It forms yellowish capillary needles, melting at 150° C. (302° F.), and subliming at about 200° C. (392° F.); nearly insoluble in water, easily soluble in boiling alcohol. When fused with potassium hydrate it yields protocatechuic acid, together with other products. The piperates even of the alkali-metals are sparingly soluble in water, the rest insoluble.

TRIATOMIC AND BIBASIC ACIDS.

The only known acids of this group are *malic acid*, $C_4H_6O_5$, and *tartronic acid*, $C_3H_4O_5$, obtained by the spontaneous decomposition of nitrotartaric acid, and perhaps also croconic acid, $C_5H_2O_5$ (p. 678).

Malic Acid, $C_4H_6O_5 = (C_4H_3O_2)'''(OH)_3$, or $\left.\begin{matrix}(C_4H_3O_2)''' \\ H \\ H\end{matrix}\right\}O_2$. — This acid is formed synthetically by the action of moist silver oxide on monobromosuccinic acid:

$$2C_4H_5BrO_4 + OAg_2 + OH_2 = 2AgBr + 2C_4H_6O_5.$$

It is also produced by the action of nitrous acid on asparagin, a substance existing in asparagus, marsh-mallow, and other plants, or on aspartic acid, an acid formed by the decomposition of asparagin under the influence of acids or alkalies:

$$\underset{\text{Asparagin.}}{C_4H_8N_2O_3} + 2NO_2H = \underset{\text{Malic acid.}}{C_4H_6O_5} + 2OH_2 + 2N_2.$$

$$\underset{\text{Aspartic acid.}}{C_4H_7NO_4} + NO_2H = \underset{\text{Malic acid.}}{C_4H_6O_5} + OH_2 + N_2.$$

Malic acid is the acid of apples, pears, and various other fruits: it is often associated with citric acid. An excellent process for preparing it is

that of Everitt, who has demonstrated its existence, in great quantity, in the juice of the common garden rhubarb: it is there accompanied by acid potassium oxalate. The rhubarb stalks are peeled, and ground or grated to pulp, which is subjected to pressure. The juice is heated to the boiling point, neutralized with potassium carbonate, and mixed with calcium acetate: insoluble calcium oxalate then falls, and may be removed by filtration. To the clear and nearly colorless liquid, solution of lead acetate is added as long as a precipitate continues to be produced; and the lead malate is collected on a filter, washed, diffused through water, and decomposed by sulphuretted hydrogen.* The filtered liquid is carefully evaporated to the consistence of a syrup, and left in a dry atmosphere until it becomes converted into a solid and somewhat crystalline mass of malic acid: regular crystals have not been obtained. From the berries of the mountain-ash (*Sorbus aucuparia*), in which malic acid is likewise present in considerable quantity, especially at the time they begin to ripen, the acid may be prepared by the same process.

Malic acid is colorless, slightly deliquescent, and very soluble in water: alcohol also dissolves it. The aqueous solution has an agreeable acid taste: it becomes mouldy and spoils by keeping. In contact with ferments, especially of putrefying cheese, it is decomposed, yielding succinic and acetic acids and carbon dioxide:

$$3C_4H_6O_5 = 2C_4H_6O_4 + C_2H_4O_2 + 2CO_2 + OH_2.$$

Sometimes also butyric acid and hydrogen are found among the products of the fermentation. Malic acid is converted into succinic acid by digesting it in sealed tubes with hydriodic acid:

$$C_4H_6O_5 + 2HI = C_4H_6O_4 + OH_2 + I_2.$$

The reconversion of succinic into malic acid has been already mentioned. The sodium-salt of bromomalic acid, $C_4H_5BrO_5$, obtained by boiling an aqueous solution of sodium dibromosuccinate ($C_4H_3NaBr_2O_4$), is converted by boiling with lime-water into the calcium-salt of tartaric acid, $C_4H_6O_6$:

$$C_4H_5BrO_5 + OH_2 = HBr + C_4H_6O_6.$$

Malic acid forms both acid and neutral salts. The most characteristic of the malates are *acid ammonium malate*, $C_4H_5O_5(NH_4)$, which crystallizes remarkably well, and *lead malate*, $C_4H_4O_5Pb''$. 3 Aq., which is insoluble in pure water, but dissolves to a considerable extent in warm dilute acids, and separates on cooling in brilliant silvery crystals, containing water. By this character the acid may be distinguished. *Acid calcium malate*, $C_4H_4O_5Ca \cdot C_4H_6O_5 \cdot 8$ Aq., is also a very beautiful salt, freely soluble in warm water. It is prepared by dissolving the sparingly soluble *neutral* malate in hot dilute nitric acid, and leaving the solution to cool.

Malic acid, as it exists in plants, and as obtained from asparagin, or from aspartic acid produced from the latter, exerts a rotatory action on polarized light; $[\alpha] = -5°$; but by the action of nitrous acid on inactive aspartic acid (resulting from the decomposition of fumarimide), Pasteur has obtained a modification of malic acid which is also optically inactive.

TRIATOMIC AND TRIBASIC ACIDS.

But few of these acids have yet been obtained; the most important are aconitic acid and carballylic acid.

* If the acid be required pure, crystallized lead malate must be used, the freshly precipitated salt invariably carrying down a quantity of lime, which cannot be removed by simple washing.

Aconitic Acid, $C_6H_6O_3 = (C_6H_3O_3)'''(OH)_3$, exists in monk's-hood (*Aconitum Napellus*), and other plants of the same genus, also in *Equisetum fluviatile*, and is one of the products obtained by the dehydration of citric acid (p. 664).

When crystallized citric acid is heated in a retort till it begins to become colored, and to undergo decomposition, and the fused, glassy product, after cooling, is dissolved in water, aconitic acid, on evaporation, remains as a white, confusedly crystalline mass, permanent in the air, and very soluble in water, alcohol, and ether; the solution has an acid and astringent taste. The salts of aconitic acid possess but little interest; that of *barium* forms an insoluble gelatinous mass; *calcium aconitate*, which has a certain degree of solubility, is found abundantly in the expressed juice of monk's-hood, and *magnesium aconitate* in that of *equisetum*.

Carballylic Acid, $C_6H_8O_6 = (C_6H_5O_3)'''(OH)_3 = (C_3H_5)'''(CO_2H)_3$, is produced by the action of nascent hydrogen on aconitic acid, and by that of alcoholic potash on propenyl tricyanide, or tricyanhydrin:

$$\underset{\text{Tricyanhydrin.}}{(C_3H_5)'''(CN)_3} + 3KOH + 3OH_2 = 3NH_3 + \underset{\text{Potassium carballylate.}}{(C_3H_5)'''(CO_2K)_3}$$

It forms colorless trimetric crystals easily soluble in water and alcohol, slightly soluble in ether. The carballylates of the alkali-metals are easily soluble in water, the rest insoluble or sparingly soluble. The *ethylic ether*, $(C_6H_5O_3)'''(OC_2H_5)_3$, is a liquid boiling between 295° and 305° C. (563°–581° F.).

TETRATOMIC ACIDS.

These acids may be derived from tetratomic alcohols by substitution of one, two, three, or four atoms of oxygen for a corresponding number of hydrogen molecules:

CH_2OH	CH_2OH	$COOH$
$\vert$	$\vert$	$\vert$
$CHOH$	$CHOH$	$CHOH$
$\vert$	$\vert$	$\vert$
$CHOH$	$CHOH$	$CHOH$
$\vert$	$\vert$	$\vert$
CH_2OH	$COOH$	$COOH$
Erythrite.	Erythric acid (monobasic).	Tartaric acid (bibasic).

Only one tetratomic acid has, however, been actually formed by oxidation of the corresponding alcohol, namely, erythric acid, $C_4H_8O_5$, from erythride, $C_4H_{10}O_4$.

The known tetratomic acids are *Gallic acid*, $C_7H_6O_5$, and *Erythric acid*, $C_4H_8O_5$, which are monobasic; *Tartaric acid*, $C_4H_6O_6$, and an acid, $C_5H_8O_6$, homologous with it, obtained by the action of moist silver oxide on dibromopyrotartaric acid, which are bibasic, and *Citric acid*, $C_6H_8O_7$, which is tribasic.

Opianic acid, $C_{10}H_{10}O_5$, *Hemipinic acid*, $C_{10}H_{10}O_6$, and *Meconic acid*, $C_7H_6O_7$, are probably also tetratomic acids; the first being monobasic, the second bibasic, and the third tribasic.

Gallic Acid, $C_7H_6O_5 = (C_7H_2O)'''(OH)_4 = (C_7\overset{H_3}{\underset{H}{H_2}}O)^{iv}\Big\}O_4$. — This acid

exists ready formed in certain plants, as sumach, hellebore root, the acorns of *Quercus ægilops*, green and black tea, and others; it is also produced by the transformation of gallo-tannic acid, and is therefore found, together with the latter, in old nut-galls. A solution of tannic acid in water exposed to the air, gradually deposits crystals of gallic acid, formed by the destruction of the tannic acid. The simplest method of preparing gallic acid in quantity is to take powdered nut-galls, which, when fresh and of good quality, contain 30 or 40 per cent. of tannic acid, with scarcely more than a trace of gallic; mix this powder with water to a thin paste, and expose the mixture to the air in a warm situation for two or three months, adding water from time to time, to replace that lost by drying up. The mouldy, dark-colored mass thus produced may then be strongly pressed in a cloth, and the solid portion boiled in a considerable quantity of water. The filtered solution deposits on cooling abundance of gallic acid, which may be drained and pressed, and finally purified by recrystallization.

Gallic acid has lately been produced by the action of moist silver oxide on dibromo-, or di-iodosalicylic acid:

$$C_7H_4Br_2O_3 + OAg_2 + OH_2 = 2AgBr + C_7H_6O_5;$$

hence it may be regarded as dioxysalicylic acid.

Gallic acid forms small, feathery, and nearly colorless crystals, which have a beautiful silky lustre; they contain $C_7H_6O_5$. Aq.; it requires for solution 100 parts of cold and only 3 parts of boiling water; the solution has an acid and astringent taste, and is gradually decomposed by keeping. Gallic acid does not precipitate gelatin; with ferrous salts it produces no change; but with ferric salts, it forms a deep bluish-black precipitate, which disappears when the liquid is heated, from the reduction of the ferric to ferrous salt at the expense of the gallic acid.

The salts of gallic acid present but little interest; those of the alkali-metals are soluble, and readily destroyed by oxidation in presence of excess of base, the solution acquiring after some time a nearly black color; the gallates of most of the other metals are insoluble.

Gallic acid heated to about 215° C. (419° F.) is resolved into carbon dioxide and pyrogallol or pyrogallic acid, $C_6H_6O_3$ (p. 570), which sublimes in crystalline plates.

Gallic acid and pyrogallic acid reduce salts of gold and silver to the metallic state: it is on this property that their application in photography depends.

When dry gallic acid is suddenly heated to 249° C. (480° F.), or above, it is decomposed into carbon dioxide, water, and *metagallic acid*, $C_6H_4O_2$, which remains in the retort as a black, shining mass, resembling charcoal; a few crystals of pyrogallic acid are formed at the same time. Metagallic acid is insoluble in water, but dissolves in alkalies, and is again precipitated as a black powder by the addition of an acid. It forms insoluble salts with lead and silver. Pyrogallic acid, also, when exposed to the requisite temperature, yields metagallic acid, with separation of water.

Appendix to Gallic Acid.

TANNIC ACIDS, OR TANNINS.

These substances constitute the astringent principles of plants, and are widely diffused, in one form or other, through the vegetable kingdom. It is possible that there may be several distinct modifications of tannic acid, which differ among themselves in some particulars. The astringent prin-

ciple of oak-bark and nut-galls, for example, is found to precipitate ferric salts bluish-black, while that from the leaves of the sumach and tea-plant, as well as infusions of the substances known in commerce under the names of *kino* and *catechu*, are remarkable for giving, under similar circumstances, precipitates which have a tint of green. The color of a precipitate is, however, too much influenced by external causes to be relied upon as a proof of essential difference. Moreover, the tannic acid or acids appear to be uncrystallizable; one most valuable test of individuality is therefore lost.

After the reaction with ferric salts, the most characteristic feature of tannic acid and the other astringent infusions referred to, is that of forming insoluble compounds with a great variety of organic, and especially animal substances, as solutions of starch and gelatin, solid muscular fibre, skin, &c., which then acquire the property of resisting putrefaction: it is on this principle that leather is manufactured. Gallic acid, on the contrary, is useless in the operation of tanning.

Tannic Acid of the Oak, Gallotannic acid, $C_{27}H_{22}O_{17}$.—This substance may be prepared by Pelouze's method, from nut-galls, which are excrescences produced on the leaves of a species of oak, the *Quercus infectoria*, by the puncture of an insect. A glass vessel,—having somewhat the figure of that represented in Fig. 195, is loosely stopped at its lower extremity by a bit of cotton wool, and half or two-thirds filled with powdered Aleppo galls. Ether, prepared in the usual manner by rectification, and containing as it invariably does a little water, is then poured upon the powder, and the vessel loosely stopped. The liquid, which after some time collects in the receiver below, consists of two distinct strata: the lower, which is almost colorless, is a very strong solution of nearly pure tannic acid in water; the upper consists of ether holding in solution gallic acid, coloring matter, and other impurities. The carefully separated heavy liquid is placed to evaporate over a surface of oil of vitriol in the vacuum of the air-pump. Tannic acid, or *tannin*, thus obtained, forms a slightly yellowish, friable, porous mass, without the slightest tendency to crystallization. It is very soluble in water, less so in alcohol, and very slightly soluble in ether. It reddens litmus and possesses a pure astringent taste without bitterness.

Fig. 195.

A strong solution of this substance mixed with mineral acids gives rise to precipitates, which consist of combinations of the tannic acid with the acids in question: the compounds are freely soluble in pure water, but nearly insoluble in acid liquids. Gallotannic acid precipitates albumin, gelatin, salts of the vegeto-alkalies, and several other substances: it forms soluble compounds with the alkalies, which, if excess of base be present, rapidly attract oxygen, and become brown by destruction of the acid; the gallotannates of *barium*, *strontium*, and *calcium* are sparingly soluble; those of *lead* and *antimony* are insoluble. Ferrous salts are unchanged by solution of gallo-tannic acid; *ferric salts*, on the contrary, give with it a deep bluish-black precipitate, which is the basis of writing-ink: hence the value of an infusion of tincture of nut-galls as a test for the presence of that metal.

Gallotannic acid, when boiled with acids, assimilates water, and splits into glucose and gallic acid:

$$\underset{\text{Gallotannic acid,}}{C_{27}H_{22}O_{17}} + 4H_2O = \underset{\text{Gallic acid,}}{3C_7H_6O_5} + \underset{\text{Glucose,}}{C_6H_{12}O_6}$$

The same reaction takes place on heating tannic acid with a concentrated solution of potash: in this case, however, the sugar is further converted into glucic acid. Nut-galls contain a ferment which induces the same decomposition of tannic acid, exciting, at the same time, alcoholic fermentation of the sugar. Gallotannic acid, prepared by the methods above mentioned, still contains a sufficient quantity of the ferment to produce this decomposition when the acid is dissolved in water, and at the ordinary temperature: it ensues, however, much more rapidly on addition of nut-galls. If this fermentation takes place in the presence of air, a part of the tannic acid is converted into *ellagic acid*, $C_{14}H_6O_8$. The same substance is found in the insoluble residue of woody fibre and other matters from which gallic acid has been withdrawn by boiling water; it may be extracted by an alkali, and afterward precipitated by addition of hydrochloric acid, as a grayish insoluble powder.

Tannic acid, closely resembling that obtained from galls, may be extracted by cold water from *catechu;* hot water dissolves out a substance having feebly acid properties, termed *catechin.* This latter compound, when pure, crystallizes in fine colorless needles, which melt when heated, and dissolve very freely in boiling water, but scarcely at all in the cold. Catechin dissolves also in hot alcohol and ether. The aqueous solution acquires a red tint by exposure to air, and precipitates lead acetate and corrosive sublimate white, reduces silver nitrate on addition of ammonia, but does not form insoluble compounds with gelatin, starch, and the vegeto-alkalies. It strikes a deep green color with ferric salts. Catechin when heated yields pyrocatechin, or oxyphenol, $C_6H_6O_2$ (p. 562). Catechin has been variously represented by the formulæ $C_9H_{10}O_4$, and $C_8H_8O_4$.

Japonic and *Rubic* acids are formed by the action of alkali in excess upon catechin, the first when the alkali is in the caustic state, and the second when it is in the state of carbonate. Japonic acid is a black and nearly insoluble substance, soluble in alkalies and precipitated by acids; it is perhaps identical with a black substance of acid properties, which Peligot obtained by heating grape-sugar with barium hydrate. Rubic acid has been but little studied: it is said to form red insoluble compounds with the earths and certain other metallic oxides.

Several acids closely allied to tannic acid have been found in coffee and Paraguay tea.

Opianic Acid, $C_{10}H_{10}O_5$, is a monobasic acid, produced, together with cotarnine, by the oxidation of narcotine:

$$\underset{\text{Narcotine.}}{C_{22}H_{23}NO_7} + O = \underset{\text{Cotarnine.}}{C_{12}H_{13}NO_3} + \underset{\text{Opianic acid.}}{C_{10}H_{10}O_5}$$

It crystallizes in thin prisms, slightly soluble in cold, easily in boiling water; also in alcohol and ether, melts at 140° C. (284° F.). Caustic potash converts it into meconin and hemipinic acid:

$$\underset{\text{Opianic acid.}}{2C_{10}H_{10}O_5} = \underset{\text{Meconin.}}{C_{10}H_{10}O_4} + \underset{\text{Hemipinic acid.}}{O_{10}H_{10}O_6}$$

TETRATOMIC AND BIBASIC ACIDS.

Tartaric Acid, $C_4H_6O_6 = (C_4H_2O_2)(OH)_4 = (C_2H_2)^{iv}\left\{\begin{matrix}(OH)_2\\(CO_2H)_2\end{matrix}\right.$. —

These formulæ include four bibasic acids distinguished from one another by certain physical properties, especially by their crystalline forms, and

their action on polarized light,—namely, *Dextrotartaric acid*, which turns the plane of polarization to the right; *Levotartaric acid*, which turns it to the left with equal force; *Paratartaric*, or *Racemic acid*, which is optically inactive, and separable into equal quantities of dextro- and levotartaric acids; and an inactive variety of tartaric acid, which is not thus separable.

Dextrotartaric or Ordinary Tartaric Acid. — This is the acid of grapes, tamarinds, pine-apples, and of several other fruits, in which it occurs in the state of an acid potassium-salt; calcium tartrate is also occasionally met with. The tartaric acid of commerce is wholly prepared from *tartar* or *argol*, an impure acid potassium tartrate, deposited from wine, or rather from grape-juice in the act of fermentation. This substance is purified by solution in hot water, with the aid of a little pipe-clay and animal charcoal, to remove the coloring matter of the wine, and subsequent crystallization: it then constitutes *cream of tartar*, and serves for the preparation of the acid. The salt is dissolved in boiling water, and powdered chalk is added as long as effervescence is excited, or the liquid exhibits an acid reaction: calcium tartrate and neutral potassium tartrate result; the latter is separated from the former, which is insoluble by filtration. The solution of potassium tartrate is then mixed with excess of calcium chloride, which throws down all the remaining acid in the form of calcium-salt: this is washed, and added to the former portion, and the whole is digested with a sufficient quantity of dilute sulphuric acid to withdraw the base, and liberate the tartaric acid. The filtered solution is cautiously evaporated to a syrupy consistence, and placed to crystallize in a warm situation. Liebig has lately found that tartaric acid is artificially produced by the action of nitric acid upon milk-sugar. It may also be obtained from succinic acid.

Succinic acid, $C_4H_6O_4$, when submitted to the action of bromine, yields two substitution-products, bromosuccinic acid, $C_4H_5BrO_4$, and dibromosuccinic acid, $C_4H_4Br_2O_4$. The latter, when treated with silver oxide in presence of water, is converted into tartaric acid and silver bromide, $C_4H_4Br_2O_4 + Ag_2O + H_2O = C_4H_6O_6 + 2AgBr$ (Perkin and Duppa; Kekulé).

Tartaric acid forms colorless, transparent crystals, often of large size, which have the figure of an oblique rhombic prism more or less modified; they are permanent in the air, and inodorous; they dissolve with great facility in water, both hot and cold, and are soluble also in alcohol. The solution reddens litmus strongly, and has a pure acid taste. The aqueous solution, as above mentioned, exhibits right-handed polarization. This solution is gradually spoiled by keeping. Tartaric acid is consumed in large quantities by the calico-printer, being employed to evolve chlorine from solution of bleaching-powder in the production of white or *discharged* patterns upon a colored ground.

Tartrates.—Tartaric acid is tetratomic and bibasic, two only of its hydrogen-atoms being replaceable by metals, the other two by alcoholic or acid radicals. With monad metals it forms acid and neutral salts, $C_4H_5M'O_6$, and $C_4H_4M_2O_6$; with dyad metals, neutral salts, $C_4H_4M''O_6$, and double salts, like *bario-potassic tartrate*, $C_4H_4Ba''O_6 . C_4H_4K_2O_6$. With triad metals it forms a peculiar class of salts, best known in the case of the *antimony-salt* (p. 675).

Potassium Tartrates. — The *neutral salt*, $C_4H_4K_2O_6$, may be procured by neutralizing cream of tartar with chalk, as in the preparation of the acid, or by adding potassium carbonate to cream of tartar to saturation; it is very soluble, and crystallizes with difficulty in right rhombic prisms, which are permanent in the air, and have a bitter, saline taste. The *acid salt*, or *cream of tartar*, $C_4H_5KO_6$, the origin and preparation of which have been

already described, forms small transparent or translucent prismatic crystals irregularly grouped together, which grate between the teeth. It dissolves pretty freely in boiling water, but the greater part separates as the solution cools, leaving about $\frac{1}{60}$ or less dissolved in the cold liquid. The salt has an acid reaction and a sour taste. When exposed to heat in a close vessel, it is decomposed, with evolution of inflammable gas, leaving a mixture of finely divided charcoal and pure potassium carbonate (black flux), from which the latter may be extracted by water. Cream of tartar is almost always produced when tartaric acid in excess is added to a moderately strong solution of a potassium-salt, and the whole agitated.

Sodium Tartrates. — Two of these salts are known — a *neutral salt*, $C_4H_4Na_2O_6 . 2\,Aq.$; and an *acid salt*, $C_4H_5NaO_6 . Aq.$ Both are easily soluble in water, and crystallizable. Tartaric acid and sodium bicarbonate form the ordinary effervescing draughts.

Potassium and sodium tartrate; Rochelle or *Seignette salt*, $C_4H_4KNaO_6 . 4\,Aq.$ This beautiful salt is made by neutralizing with sodium carbonate a hot solution of cream of tartar, and evaporating to the consistence of thin syrup. It separates in large, transparent, prismatic crystals, the faces of which are unequally developed: these effloresce slightly in the air, and dissolve in $1\frac{1}{2}$ parts of cold water. Acids precipitate cream of tartar from the solution. Rochelle salt has a mild saline taste, and is used as a purgative.

Ammonium Tartrates. — The *neutral tartrate* is a soluble and efflorescent salt, containing $C_4H_4(NH_4)_2O_6 . Aq.$ The *acid tartrate*, $C_4H_5(NH_4)O_6$, closely resembles ordinary cream of tartar. A salt corresponding to Rochelle salt also exists, having ammonium in place of sodium.

The tartrates of *calcium*, *barium*, *strontium*, *magnesium*, and of most of the heavy metals, are insoluble, or nearly so, in water.

Potassio-antimonious Tartrate, or *tartar emetic*, is easily made by boiling antimony trioxide in solution of cream of tartar: it is deposited from a hot and concentrated solution in crystals derived from an octohedron with rhombic base, which dissolve without decomposition in 15 parts of cold and 3 of boiling water, and have an acrid and extremely disagreeable metallic taste. The solution is decomposed by both acids and alkalies: the former throws down a mixture of cream of tartar and antimony trioxide, and the latter the trioxide, which is again dissolved by great excess of the reagent. Sulphuretted hydrogen separates all the antimony in the state of trisulphide. The dry salt heated on charcoal before the blowpipe, yields a globule of metallic antimony. The crystals contain $2C_4H_4K(SbO)O_6 . Aq.$, the group SbO acting as a univalent radical, and replacing one atom of hydrogen. When dried at 100°, they give off their water of crystallization, and at 200° C. (392° F.), an additional molecule of water, leaving the compound $C_4H_2K(SbO)O_5$, which has the constitution of a salt, not of tartaric, but of tartrelic acid, $C_4H_4O_5$. Nevertheless, when dissolved in water, the crystals again take up the elements of water, and reproduce the original salt.

An analogous compound, containing arsenic in place of antimony, has been described. It has the same crystalline form as tartar emetic.

A solution of tartaric acid dissolves ferric hydrate in large quantity, forming a brown liquid, which has an acid reaction, and dries up by gentle heat to a brown, transparent, glassy substance, destitute of all traces of crystallization. It is very soluble in water, and the solution is not precipitated by alkalies, either fixed or volatile. Indeed, tartaric acid, added in sufficient quantity to a solution of ferric oxide, or alumina, entirely prevents the precipitation of the bases by excess of ammonia. Tartrate and ammoniacal tartrate of iron are used in medicine, these compounds having a less disagreeable taste than most of the iron preparations.

Solutions of tartaric acid give with lime and baryta-water, and with lead acetate, white precipitates, which dissolve in excess of the acid; with neutral calcium and barium-salts no change is produced. Silver nitrate produces in neutral tartrates a white precipitate of silver tartrate, which dissolves in ammonia. On gently heating the solution, a bright metallic deposit of silver is formed. The reaction of tartaric acid with solutions of potassium-salts has been already noticed (p. 299).

Tartaric Ethers. — 1. Tartaric acid forms, with monatomic alcohol-radicals, acid and neutral ethers, in which one or both of the atoms of *basic* hydrogen in its molecule is replaced by an alcohol-radical. These compounds may be conveniently formulated as follows:

$(C_2H_2)^{iv}\{(OH)_2, (CO_2H)_2$ — Tartaric acid.

$(C_2H_2)^{iv}\{(OH)_2, CO_2H, CO_2C_2H_5$ — Acid ethyl tartrate.

$(C_2H_2)^{iv}\{(OH)_2, (CO_2C_2H_5)_2$ — Neutral ethyl tartrate.

The acid ethers are monobasic acids, formed by the direct action of tartaric acid on the respective alcohols; the neutral ethers are formed by passing hydrochloric acid gas into a solution of tartaric acid in an alcohol. Further, by treating these neutral ethers with chlorides of acid radicals, other neutral ethers are formed, in which one or more of the alcoholic hydrogen-atoms are replaced by acid radicals.* In this manner are formed such compounds as the following:

$(C_2H_2)^{iv}\{OH, OC_2H_3O, (CO_2C_2H_5)_2$ — Ethyl aceto-tartrate.

$(C_2H_2)^{iv}\{OC_2H_3O, OC_7H_5O, (CO_2C_2H_5)_2$ — Ethyl aceto-benzo-tartrate.

$(C_2H_2)^{iv}_{(C_2H_2)^{iv}}\{(OH)_2, (O_2C_4H_4O_2)'', (CO_2C_2H_5)_4$ — Ethyl succino-tartrate.

The alcoholic hydrogen in these neutral ethers may be replaced by potassium and sodium.

2. There are also *bibasic tartaric ethers* formed by replacing the alcoholic hydrogen of tartaric acid with acid radicals; *e. g.:*

$(C_2H_2)^{iv}\{OH, OC_7H_5O, (CO_2H)_2$ — Benzotartaric acid.

$(C_2H_2)^{iv}\{(OC_2H_3O)_2, (CO_2H)_2$ — Diacetotartaric acid.

$(C_2H_2)_{iv}\{(NO_2)_2, (CO_2H)_2$ — Dinitrotartaric acid.

3. Lastly, tartaric acid forms ethers with glycol, glycerin, mannite, glucose, and other polyatomic alcohols.

Action of heat on Tartaric Acid. — When crystallized tartaric acid is exposed to a temperature of about 204° C. (399° F.), it melts, loses water, and yields in succession three different anhydrides, viz.:

Ditartaric or Tartralic acid . . $C_8H_{10}O_{11} = 2C_4H_6O_6 - H_2O$

Tartrelic acid . . . . } $C_4H_4O_5 = C_4H_6O_6 - H_2O$

Insoluble tartaric anhydride . }

The first two are soluble in water, and form salts which have properties completely different from those of ordinary tartaric acid. The third is a white insoluble powder. All three, in contact with water, slowly pass into ordinary tartaric acid.

Tartaric acid, subjected to destructive distillation, is resolved into carbon dioxide and pyrotartaric acid, $C_3H_6O_4$.

When tartaric acid is heated to 204·5° C. (400° F.), with excess of potas-

* *Perkin*, Chem. Soc. Jour. [2], v. 139.

sium hydrate, it is resolved, without charring or secondary decomposition, into oxalic and acetic acids, which remain in union with the base, and only undergo decomposition at a much higher temperature:

$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} + 2KHO = \underset{\text{Acid potassium oxalate.}}{C_2KHO_4} + \underset{\text{Potassium acetate.}}{C_2H_3KO_2} + 2OH_2$$

Paratartaric or Racemic Acid.—The grapes cultivated in certain districts of the Upper Rhine, and also in the Vosges, contain, in association with tartaric acid, another acid body to which the above names are given. This acid is rather less soluble than tartaric acid, and separates first from the solution of that substance. Between these two acids, however, a very great resemblance exists; they have exactly the same composition, and yield, when exposed to heat, the same products; the salts of racemic acid correspond also, in the closest manner, with the tartrates. A solution of racemic acid, however, precipitates a neutral calcium-salt, which is not the case with tartaric acid. A solution of racemic acid does not rotate the plane of polarization.

Racemic acid has been the subject of some exceedingly interesting researches by M. Pasteur, which have thrown much light upon the relation of this acid to tartaric acid. If racemic acid be saturated with potash, or soda, or with most other bases, crystals are obtained, which are identical in form and physical properties. By saturating racemic acid, however, with two bases, by forming, for instance, compounds corresponding to Rochelle salt, which contain potassium and sodium, or ammonium and sodium, and allowing the solution to crystallize slowly, two varieties of crystals are produced, which may be distinguished by their form, each of them containing hemihedral faces (p. 263), equal in number and exactly similar in form, but developed on opposite sides of the two crystals, so that each of them may be regarded as the reflected image of the other, or as right-handed and left-handed. If the two kinds of crystals are carefully selected and separately crystallized, crystals of the one variety only are deposited in each case. The composition, the specific gravity, and, in fact, most of the physical properties of these two varieties of sodio-potassic racemate, are invariably the same They differ, however, somewhat in their chemical characters, and especially in one point: they rotate the plane of polarization in opposite directions. Pasteur assumes, in the two varieties of crystals, the existence of two modifications of the same acid, which he distinguishes, according as the salt possesses right- or left-handed polarization, by the terms *dextro-racemic* and *levo-racemic*, or *dextro-* and *levo-tartaric acids*. These acids may be separated by converting the above compounds into lead- or barium-salts, and decomposing them by means of sulphuric acid. In this manner two crystalline acids are obtained, identical in every respect, excepting in their deportment with polarized light, and in their crystals being related to each other in the manner above mentioned. Dextrotartaric acid is nothing but common tartaric acid. A mixture of equal parts of the two acids has no longer the slightest effect on polarized light, and exhibits in every respect the deportment of racemic acid.

Pasteur, in continuing his beautiful researches, has also made the important discovery that racemic acid may be artificially produced by the action of heat upon certain compounds of tartaric acid which are capable of resisting a high temperature. When tartrate of cinchonine * or tartaric ether, is exposed to a temperature of about 170° C. (338° F.), and the product thus formed is repeatedly boiled with water, a solution is obtained, which, when mixed, after cooling, with an excess of calcium chloride, yields a con-

* See the chapter on Organic Bases.

siderable precipitate of calcium racemate. Compounds of levotartaric acid, when submitted to the action of heat, likewise furnish racemic acid. The formation of racemic acid in these reactions is accompanied by the production of a fourth modification of tartaric acid, which Pasteur calls inactive tartaric acid. Like racemic acid, it has no action on polarized light, but cannot, like the latter, be resolved into levo- and dextrotartaric acid.

Rhodizonic Acid, $C_5H_4O_6$.—When potassium is heated in a stream of dry carbon monoxide, the latter is absorbed in large quantity, and a black porous substance generated, which, according to Brodie, contains COK_2. Brought in contact with water, it decomposes with great violence, and even the dry substance occasionally explodes; when anhydrous alcohol is poured upon it, a great elevation of temperature ensues, but the decomposition is far less violent than with water. The product of this reaction is potassium rhodizonate, which remains as a red powder, insoluble in alcohol, but soluble in water with a deep red color. This salt probably contains $C_5H_2K_2O_6$.

When solution of potassium rhodizonate is boiled, it becomes orange-yellow from decomposition of the acid, and is then found to contain a free potash, and a salt of *Croconic acid*, $C_5H_2O_5$. This acid can be isolated: it is yellow, easily crystallizable, soluble both in water and alcohol. It is likewise bibasic.

TETRATOMIC AND TRIBASIC ACIDS.

Citric Acid, $C_6H_8O_7$.—This acid is obtained in large quantities from the juice of lemons: it is found in many other fruits, as in gooseberries, currants, &c., in conjunction with malic acid. In the preparation of this acid, the juice is allowed to ferment a short time, in order that mucilage and other impurities may separate and subside: the clear liquor is then carefully saturated with chalk, whereby insoluble calcium citrate is produced. This is thoroughly washed, decomposed by the proper quantity of sulphuric acid, diluted with water, and the filtered solution is evaporated to a small bulk, and left to crystallize. The product is drained from the mother-liquor, redissolved, digested with animal charcoal, and again concentrated to the crystallizing point.

Citric acid crystallizes in two different forms. The crystals which separate by spontaneous evaporation from a cold saturated solution, are trimetric prisms, containing $C_6H_8O_7 . OH_2$, whereas those which are deposited from a hot solution have a different form and contain $2C_6H_8O_7 . OH_2$. — Citric acid has a pure and agreeable acid taste, and dissolves, with great ease, in both hot and cold water; the solution strongly reddens litmus, and, when long kept, is subject to spontaneous change. Citric acid, when brought in contact with putrid flesh as a ferment, yields butyric acid and small quantities of succinic acid. It is entirely decomposed when heated with sulphuric and nitric acids: the latter converts it into oxalic acid. Caustic potash, at a high temperature, resolves it into acetic and oxalic acids. The alkaline citrates, treated with chlorine, yield chloroform, together with other products.

Citric acid is tetratomic and tribasic, and may be represented by the formula $(C_3H_4)^{iv}\left\{\begin{matrix}OH\\(CO_2H)_3,\end{matrix}\right.$ or $C^{iv}\left\{\begin{matrix}CH_2OH\\H_2\\(CO_2H)_3\end{matrix}\right.$. It has not yet been obtained by any synthetical process. With *potassium* it forms a neutral salt

containing $C_6H_5K_3O_7$, and two acid salts containing respectively $C_6H_6K_2O_7$ and $C_6H_7KO_7$; and similar salts with the other alkali-metals. With dyad metals it chiefly forms salts in which two or three hydrogen-atoms in the molecule $C_6H_8O_7$, are replaced by metals; with *calcium*, for example, it forms the salts $C_6H_6Cu''O_7$. Aq., and $(C_6H_5O_7)_2Ca''_3$. Aq. With *lead* it forms two salts similar in constitution to the calcium-salts, and likewise a tetraplumbic salt containing $(C_6H_5O_7)_2Pb''_3 . Pb''H_2O_2$.

The citrates of the *alkali-metals* are soluble and crystallize with greater or less facility; those of *barium, strontium, calcium, lead,* and *silver* are insoluble.

Citric acid resembles tartaric acid in its relations to ferric oxide, preventing the precipitation of that substance by excess of ammonia. The citrate obtained by dissolving hydrated ferric oxide in solution of citric acid, dries up to a pale-brown, transparent, amorphous mass, which is not very soluble in water; an addition of ammonia increases the solubility. Citrate and ammonia-citrate of iron are elegant medicinal preparations. Very little is known respecting the composition of these curious compounds: the absence of crystallization is a great bar to exact inquiry.

Citric acid is sometimes adulterated with tartaric acid: the fraud is easily detected by dissolving the acid in a little cold water, and adding to the solution a small quantity of potassium acetate. If tartaric acid be present, a white crystalline precipitate of cream of tartar will be produced on agitation.

Citric acid forms ethers in which 1, 2, or 3 hydrogen-atoms are replaced by methyl and other monad alcohol-radicals.

Meconic Acid, $C_7H_4O_7$, a tribasic acid existing in opium, may also be described here. To prepare it, the liquid obtained by exhausting opium with water, is neutralized with powdered marble and precipitated by calcium chloride; and the calcium meconate thus precipitated is suspended in warm water and treated with hydrochloric acid; on cooling, impure meconic acid crystallizes, which may be purified by repeated treatment with hydrochloric acid. The pure acid crystallizes in mica-like plates, easily soluble in boiling, difficultly soluble in cold water, soluble likewise in alcohol. The crystals contain $C_7H_4O_7 . 3$ Aq. and give off their water at 100°. The *meconates* are, for the most part, mono- and bi-metallic. There are two *silver meconates*, one yellow, containing $C_7HAg_3O_7$; the other white, consisting of $C_7H_2Ag_2O_7$. Meconic acid produces a deep red color with ferric salts.

Comenic Acid, $C_6H_4O_5$, is a product of decomposition of meconic acid. When an aqueous, or, better, a hydrochloric solution of meconic acid is boiled, carbon dioxide is evolved, and the solution now contains comenic acid, which crystallizes on cooling, being very difficultly soluble in cold water. The same acid may be obtained by heating meconic acid to 200° C. (392° F.). It is bibasic: its formation is represented by the equation $C_7H_4O_7 = C_6H_4O_5 + CO_2$.

Pyromeconic or Pyrocomenic Acid, $C_5H_4O_3$, is a monobasic acid, formed by submitting either comenic or meconic acid to dry distillation, one molecule of carbon dioxide being evolved in the former case and two in the latter.

Pyrocomenic acid is a weak acid: it is soluble in water and alcohol: from these solutions it crystallizes in long colorless needles, which melt at 120° C. (248° F.), and begin to sublime at the boiling point of water. Both comenic and pyrocomenic acids exhibit the red coloration with ferric salts.

The salts of meconic acid and comenic acid, together with several deriva-

tives of these substances, have been studied by Mr. How,* but our space will not permit us to describe these compounds.

An acid much resembling m[illegible] acid has been extracted from the *Chelidonium majus:* it is combined with lime, and associated with malic and fumaric acids. Chelidonic acid is tribasic, forming three classes of salts. When exposed to a high temperature, it yields a pyro-acid, with evolution of water and carbon dioxide. It crystallizes in slender colorless easily soluble needles, containing $C_7H_4O_5 . Aq$.

PENTATOMIC ACIDS.

There is but one known acid that can be referred to this group, namely:

Quinic or **Kinic Acid**, $C_7H_{12}O_6$, which is monobasic, and may perhaps be represented by the formula $(C_6H_7)'\left\{\begin{matrix}(OH)_4\\CO_2H\end{matrix}\right.$.—The calcium-salt of this acid is found in the solution from which the alkalies of cinchona bark have been separated by lime, and is easily obtained by evaporation, and purified by animal charcoal. From the calcium-salt the acid may be extracted by decomposing it with dilute sulphuric acid. The clear solution evaporated to a syrupy consistence deposits large, distinct crystals, resembling those of tartaric acid, and soluble in 2 parts of water. Quinic acid has also been found in coffee-berries and in the leaves of the bilberry-bush.

When quinic acid is heated with a mixture of sulphuric acid and manganese dioxide, it yields a very volatile substance termed *quinone*, the vapor of which is exceedingly irritating to the eyes. This body forms crystals, both by sublimation and by solution in boiling water: it melts at a gentle heat, crystallizes on cooling, colors the skin permanently brown. It contains $C_6H_4O_2$, and its formation is represented by the equation:

$$C_7H_{12}O_6 + O_2 = C_6H_4O_2 + CO_2 + 4H_2O.$$

By destructive distillation, quinic acid yields numerous and interesting products, which have been studied by Wöhler, as benzoic acid, phenol, salicylol, benzene, a tarry substance not examined, and *colorless hydroquinone*, $C_6H_6O_2$, containing 2 atoms of hydrogen more than quinone. This substance forms colorless six-sided prismatic crystals; it is neutral, destitute of taste and odor, fusible, and easily soluble both in water and in alcohol.

Colorless hydroquinone can be easily and directly produced from quinone by assimilation of hydrogen, as by addition of hydriodic acid to a solution of the latter, iodine being then set free, or by sulphurous acid.

An intermediate product of reduction is *green hydroquinone*, or *quinhydrone*, $C_{12}H_{10}O_4$. This is obtained by the incomplete action of sulphurous acid upon quinone, or by the action of ferric chloride, chlorine, silver nitrate, or chromic acid, upon colorless hydroquinone; or by mixing together solutions of quinone and colorless hydroquinone. It forms slender green crystals, having the color of the wing-case of the rose-beetle, and of the greatest brilliancy and beauty. It is fusible, has but little odor, and dissolves freely in boiling water, crystallizing out on cooling.

If quinic acid be submitted to distillation with an ordinary chlorine-mixture, an acid liquid and a crystalline sublimate are formed. The former is a solution of formic acid, and the latter a mixture of four chlorinetted compounds, which are chloroquinone, $C_6H_3ClO_2$, dichloroquinone, $C_6H_2Cl_2O_2$, trichloroquinone, $C_6HCl_3O_2$, and tetrachloroquinone, $C_6Cl_4O_2$. They are all

* Chem. Soc. Quar. Journal, iv. 363.

yellow crystalline substances, which can be separated only with great difficulty. Like quinone itself, they possess the faculty of combining with 1 or 2 atoms of hydrogen, producing two series of substances analogous to green and colorless hydroquinone. Tetrachloroquinone, better known by the name *chloranil*, likewise occurs among the products of decomposition of indigo.

Other products are obtained by the action of sulphuretted hydrogen and strong hydrochloric acid upon quinone.

HEXATOMIC ACIDS.

Three acids of this class are known; namely, mannitic, saccharic, and mucic acids, all of which appear to be bibasic.

Mannitic Acid, $C_6H_{12}O_7$, is produced by oxidation of mannite, $C_6H_{14}O_6$, under the influence of platinum black. It is a gummy mass, soluble in water and in alcohol, insoluble in ether. According to its constitution (p. 573) it might be expected to be monobasic, but from the observations of Gorup-Besanez, who discovered it,* it appears to be bibasic, its potassium-salt containing $C_6H_{10}K_2O_7$, and the calcium-salt, $C_6H_{10}Ca''O_7$.

Saccharic Acid, $C_6H_{10}O_8 = (C_4H_4)^{vi}\left\{\begin{matrix}(OH)_4\\(CO_2H)_2\end{matrix}\right.$. — This acid is produced by the action of dilute nitric acid on cane-sugar, glucose, milk-sugar, and mannite, and is often formed in the preparation of oxalic acid, being, from its superior solubility, found in the mother-liquor from which the oxalic acid has crystallized. It may be made by heating together 1 part of sugar, 2 parts of nitric acid, and 10 parts of water. When the reaction seems terminated, the acid liquid is diluted, neutralized with chalk, and the filtered liquid is mixed with lead acetate. The insoluble lead saccharate is washed, and decomposed by sulphuretted hydrogen. The acid slowly crystallizes from a solution of syrupy consistence in long colorless needles; it has a sour taste, and forms soluble salts with lime and baryta. When mixed with silver nitrate it gives no precipitate, but, on the addition of ammonia, a white insoluble substance separates, which is reduced by gently warming the whole to metallic silver, the vessel being lined with a smooth and brilliant coating of the metal. Nitric acid converts saccharic into oxalic acid.

There are two *potassium saccharates*, containing $C_6H_9KO_8$ and $C_6H_8K_2O_8$; the *silver-salt* contains $C_6H_8Ag_2O_8$; the *barium*, *magnesium*, *zinc*, and *cadmium salts* have the composition $C_6H_8M''O$; and there are two *ethylic ethers*, containing $C_6H_9(C_2H_5)O_8$ and $C_6H_8(C_2H_5)_2O_8$. In these compounds saccharic acid appears to be bibasic, as might be expected from its mode of formation (p 573); the composition of the lead-salts, however, seems to show that it is sexbasic as well as hexatomic, for Heintz has obtained a lead-salt containing $C_6H_4Pb''_3O_8$; but the composition of the lead saccharates varies considerably according to the manner in which they are prepared.

Mucic Acid, $C_6H_{10}O_8$.—This acid, isomeric with saccharic acid, is produced, together with a small quantity of oxalic acid, by the action of rather dilute nitric acid on sugar and gum. It may be easily prepared by heating together in a flask or retort, 1 part of milk-sugar or gum, 4 parts of nitric acid, and 1 part of water; the mucic acid is afterwards collected upon a filter, washed and dried. It has a slightly sour taste, and reddens vegetable

* Ann. Ch. Pharm. cxviii. 257.

colors. It requires for solution 66 parts of boiling water. Oil of vitriol dissolves it, with production of a red color. Mucic acid is decomposed by heat, yielding, among other products, *pyromucic acid*, $C_5H_4O_6$, which is volatile, soluble in water, and crystallizes in a form resembling that of benzoic acid.

Mucic acid is bibasic, yielding for the most part neutral salts containing $C_6H_8M_2O_8$ and $C_6H_8M''O_8$; with the alkali-metals it also forms acid salts, such as $C_6H_9KO_8$. There are also mucic ethers, containing one and two equivalents of monad alcohol-radical.

SULPHO-ACIDS.

This name is applied to a group of acids formed from hydrocarbons, alcohols, acids, and amides, by the action of fuming sulphuric acid or sulphuric oxide. They contain the elements of a hydrocarbon, an alcohol, or an acid, combined with one or two molecules of sulphuric oxide, and may be regarded as derived from hydrocarbons, alcohols, and acids by substitution of the univalent radical, SO_3H, for hydrogen; thus, sulphacetic acid, $C_2H_4SO_5$, has the composition:

$$C_2H_4O_2 . SO_3, \text{ or } CH_2(SO_3H) . CO_2H, \text{ or } \begin{matrix} H_2C—S—O—O—OH \\ | \\ O = C—OH. \end{matrix}$$

The sulphur in these acids is in immediate combination with the carbon; in this respect they differ from sulphuric ethers (p. 509), in which the sulphur is united with carbon only through the medium of oxygen.

Sulphacetic Acid is produced by digesting glacial acetic acid with sulphuric oxide at 60°–75° C. (140°–167° F.) for several days. The aqueous solution of the mass saturated with barium or lead carbonate deposits a crystalline barium or lead-salt, containing respectively $C_2H_2Ba''SO_5 . 1\frac{1}{2}$ Aq. and $C_2H_2Pb''SO_5$. From these salts the acid may be obtained by means of sulphuric or sulph-hydric acid. It is bibasic, since it contains two equivalents of hydroxyl in immediate association with oxygen, one belonging to the group CO_2H, the other to the group SO_3H.

When sulphacetic acid is subjected to the prolonged action of fuming sulphuric acid, carbon dioxide is evolved, and *disulphometholic* or *methionic acid*, $CH_4(SO_3)_2$, or $CH_2(SO_3H)_2$, is formed, which is also bibasic, and may be derived from methane, CH_4, by substitution of $2SO_3H$ for H_2. The product diluted with water and saturated with barium carbonate, yields a beautifully crystallized, and rather sparingly soluble barium-salt, containing $CH_2S_2O_6Ba''$; from this salt the acid may be separated by sulphuric acid.

Both sulphacetic and disulphometholic acids may be produced by the action of fuming sulphuric acid on acetamide or on acetonitrile, the former when the mixture is kept cool, the latter when the temperature is allowed to rise, carbon dioxide being then given off; thus:

$$\underset{\text{Acetonitrile.}}{C_2H_3N} + OH_2 + \underset{\text{Sulphuric acid.}}{2SO_4H_2} = \underset{\text{Acid ammonium sulphate.}}{SO_4H(NH_4)} + \underset{\text{Sulphacetic acid.}}{C_2H_4SO_5}$$

$$\underset{\text{Acetonitrile.}}{C_2H_3N} + 3SO_4H_2 = SO_4H(NH_4) + \underset{\text{Disulphometholic acid.}}{CH_4S_2O_6} + CO_2$$

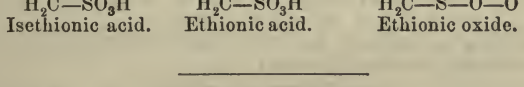
With acetamide, $C_2H_3ONH_2$, which differs from acetonitrile only by the elements of water, the two reactions are exactly similar.

Sulphopropionic Acid, $C_2H_4(SO_3H) . CO_2H$, and Disulphetholic Acid, $C_2H_4(SO_3H)_2$, are prepared in the same way from propionic acid, propionamide, or propionitrile.

Sulphobenzoic Acid, $C_6H_4(SO_3H) . CO_2H$, is produced by the action of sulphuric oxide on benzoic acid; also, together with disulphobenzolic acid, $C_6H_4(SO_3H)_2$, by that of fuming sulphuric acid on benzonitrile or phenyl cyanide, C_7H_5N. Both are bibasic. *Sulphobenzolic acid*, $C_6H_5(SO_3H)$, is produced, together with sulphobenzide, $C_{12}H_{10}SO_2$, by the action of sulphuric oxide on benzene. On mixing the resulting viscid liquid with a large quantity of water, the sulphobenzide is precipitated as a crystalline powder, while sulphobenzolic acid remains in solution, and may be obtained in the crystalline form by converting it into a copper-salt, decomposing the latter with sulphuretted hydrogen, and evaporating. It is monobasic, and forms soluble salts with the alkali-metals, barium, iron, copper, and silver. By the prolonged action of fuming sulphuric acid, it is converted into *disulphobenzolic acid*, $C_6H_4(SO_3H)_2$.

Sulphonaphthalic Acid, $C_{10}H_7(SO_3H)$, and Disulphonaphthalic Acid, $C_{10}H_6(SO_3H)_2$, are produced by melting naphthalene with strong sulphuric acid or sulphuric oxide. By neutralizing the aqueous solution of the product with barium carbonate, concentrating, and adding alcohol, the disulphonaphthalate of barium is precipitated, while the sulphonaphthalate remains dissolved. By using a large excess of sulphuric acid, and applying a strong heat, nearly the whole of the naphthalene is converted into disulphonaphthalic acid. Both these acids are crystalline, and form soluble and crystallizable salts; sulphonaphthalic acid is monobasic; disulphonaphthalic acid bibasic.

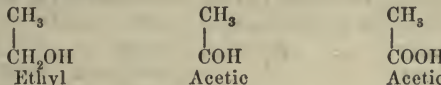
Isethionic acid, $C_2H_6SO_4$, *ethionic acid*, $C_2H_6S_2O_7$, and *ethionic oxide*, or *anhydride*, $C_2H_4S_2O_6$, produced, as already mentioned (pp. 518, 527), by the action of sulphuric oxide, or fuming sulphuric acid, on alcohol and ether, likewise belong to this class of bodies, and may be represented by the following formulæ, which show that isethionic acid is monobasic, ethionic acid bibasic, and ethionic oxide neutral:



Isethionic acid. Ethionic acid. Ethionic oxide.

ALDEHYDES.

These are bodies derived from alcohols by elimination of one or more molecules of hydrogen (H_2), without introduction of an equivalent quantity of oxygen, so that they hold a position intermediate between the alcohols and the acids; thus:



Ethyl alcohol. Acetic aldehyde. Acetic acid.

The hydrogen eliminated in the conversion of an alcohol into an acid is that which is in immediate connection with the hydroxyl, or which belongs to the group CH_2OH; consequently a monatomic alcohol can yield but one aldehyde; but a diatomic alcohol can yield two, by substitution of O for H_2, and of O_2 for $2H_2$; a triatomic alcohol three, and so on. At present, however, we are acquainted only with aldehydes derived from monatomic and diatomic alcohols.

Aldehydes derived from Monatomic Alcohols.

Of these aldehydes four series are known, viz.:

1. *Aldehydes*, $C_nH_{2n}O$, *corresponding to the Fatty acids.*

Formic aldehyde	CH_2O	Caproic aldehyde	$C_6H_{12}O$
Acetic aldehyde	C_2H_4O	Œnanthylic aldehyde	$C_7H_{14}O$
Propionic aldehyde	C_3H_6O	Caprylic aldehyde	$C_8H_{16}O$
Butyric aldehyde	C_4H_8O	Euodic aldehyde	$C_{11}H_{22}O$.
Valeric aldehyde	$C_5H_{10}O$		

2. *Aldehydes*, $C_nH_{2n-2}O$, *corresponding to the Acrylic acids.*

Acrylic aldehyde, or Acrolein	C_3H_4O.

3. *Aldehydes*, $C_nH_{2n-8}O$, *corresponding to the Aromatic acids.*

Benzoic aldehyde, or Bitter-almond oil	C_7H_6O
Toluic aldehyde	C_8H_8O
Cumic aldehyde	$C_{10}H_{12}O$
Sycocerylic aldehyde	$C_{18}H_{28}O$.

4. *Aldehydes*, $C_nH_{2n-10}O$.

Cinnamic aldehyde	C_9H_8O.

All these aldehydes contain two atoms of hydrogen less than the corresponding alcohols, and one atom of oxygen less than the corresponding acids.

They are produced:—1. By oxidation of alcohols, either by the action of atmospheric oxygen, or by that of a mixture of dilute sulphuric acid and potassium bichromate or manganese dioxide, or by the action of chlorine on the alcohol diluted with water, the chlorine in this case decomposing the water, and thus acting as an oxidizing agent.

2. By distilling an intimate mixture of the potassium-salt of the corresponding acid with potassium formate; *e. g.*:

$COCH_3(OK)$ Potassium acetate.	+	$COH(OK)$ Potassium formate.	=	$CO(OK)_2$ Potassium carbonate.	+	$CH_3.COH$ Acetic aldehyde.
$COC_6H_5(OK)$ Potassium benzoate.	+	$COH(OK)$	=	$CO(OK)_2$	+	$C_6H_5.COH$ Benzoic aldehyde.

3. By the action of nascent hydrogen (evolved by the action of dry hydrochloric acid gas on sodium amalgam) on the cyanides of acid radicals:

C_7H_5OCN Benzoyl cyanide.	+	H_2	=	CNH Hydrocyanic acid.	+	C_7H_6O Benzoic aldehyde.

Properties. — The following properties are common to all the monatomic aldehydes:

1. They easily take up *oxygen*, and are converted into the corresponding acids.

2. When fused with *potash*, they are converted into the corresponding acids, with evolution of hydrogen: *e. g.:*

$$\underset{\text{Benzoic aldehyde.}}{C_7H_6O} + KOH = \underset{\text{Potassium benzoate.}}{C_7H_5KO_2} + H_2.$$

3. *Nascent hydrogen*, evolved by the action of water on sodium amalgam, converts them into the corresponding alcohols; *e. g.*, $C_2H_4O + H_2 = C_2H_6O$. If, however, the aldehyde belongs to a non-saturated series, the action goes further, an additional quantity of hydrogen being then taken up, whereby the alcohol first formed is converted into a saturated alcohol belonging to another series; thus:

$$\underset{\text{Acrylic aldehyde.}}{C_3H_4O} + H_2 = \underset{\text{Allyl alcohol.}}{C_3H_6O}; \text{ and } \underset{\text{Allyl alcohol.}}{C_3H_6O} + H_2 = \underset{\text{Propyl alcohol.}}{C_3H_8O}$$

Nascent hydrogen evolved by the action of zinc on sulphuric acid does not appear to unite with aldehydes.

4. *Phosphorus pentachloride* converts aldehydes into chloraldehydes, compounds derived from aldehydes by substitution of Cl_2 for O; thus:

$$\underset{\text{Aldehyde.}}{\begin{matrix}CH_3\\|\\COH\end{matrix}} + PCl_5 = PCl_3O + \underset{\text{Chloraldehyde.}}{\begin{matrix}CH_3\\|\\CHCl_2\end{matrix}}$$

The compounds thus produced are isomeric with the chlorides of the olefines; *e. g.*, acetic chloraldehyde, $CH_3.CHCl_2$, or ethidene chloride, with ethene chloride, $C_2H_4.Cl_2$ (p. 484).

5. *Chlorine* and *bromine* convert aldehydes into chlorides of acid radicals:

$$\underset{\text{Aldehyde.}}{C_2H_4O} + Cl_2 = HCl + \underset{\text{Acetyl chloride.}}{C_2H_3O.Cl}$$

$$\underset{\text{Aldehyde.}}{C_2H_4O} + 2Cl_2 = 2HCl + \underset{\text{Chloracetyl chloride.}}{C_2H_2ClO.Cl}$$

6. The *alkali-metals* dissolve in aldehydes, eliminating an equivalent quantity of hydrogen:

$$\underset{\text{Aldehyde.}}{2C_2H_4O} + K_2 = H_2 + \underset{\text{Potassium aldehyde.}}{2C_2H_3KO}$$

7. Aldehydes treated with *hydrocyanic acid*, *hydrochloric acid*, and *water*, are converted into an ammonium-salt, or an amidated acid, containing an additional atom of carbon, the former reaction taking place chiefly in the aromatic series, the latter in the fatty series:

$$\underset{\text{Acetic aldehyde.}}{C_2H_4O} + CNH + OH_2 = \underset{\text{Amidopropionic acid (alanine).}}{C_3H_7NO_2}$$

$$\underset{\text{Benzoic aldehyde.}}{C_7H_6O} + CNH + 2OH_2 = \underset{\text{Ammonium formobenzoate.}}{C_8H_7(NH_4)O_3}$$

8. Aldehydes unite with *aniline*, water being eliminated, and form bases derived from a double molecule of aniline, $(C_6H_7N)_2$, by substitution of two equivalents of a diatomic radical for four atoms of hydrogen; *e. g.*:

$$\underset{\text{Acetic aldehyde.}}{(C_2H_4O)_2} + \underset{\text{Aniline.}}{2C_6H_7N} = 2OH_2 + \underset{\text{Diethidene-dianiline.}}{C_{12}H_{10}(C_2H_4)''_2N_2}$$

9. All aldehydes unite directly with the *acid sulphites of the alkali-metals*, forming crystalline compounds, by which they may be readily separated from other bodies with which they may be mixed. This reaction affords a ready means of purifying aldehydes, and likewise of detecting their presence.

10. Aldehydes also unite with *acetic oxide*, forming such compounds as $C_2H_4O''(C_2H_3O)_2$, and probably with the oxides corresponding to other monobasic acids.

Aldehydes belonging to the Series $C_nH_{2n}O$.

Formic Aldehyde, CH_2O or H . COH, also called *Methylic aldehyde.*—This compound, recently discovered by Hofmann,* is produced when a current of air charged with vapor of methyl alcohol is directed upon an incandescent spiral of platinum wire; and by suitable condensing arrangements, a liquid may be obtained consisting of a solution of the aldehyde in methyl alcohol. This liquid, rendered slightly alkaline by ammonia, and gently warmed with silver nitrate, yields a beautiful specular deposit of silver, with greater ease even than ordinary acetic aldehyde. The same solution, heated with a few drops of caustic potash, deposits drops of a brownish oil, having the odor of the resin of acetic aldehyde.

Formic aldehyde has not yet been obtained in the pure state; but by treating its solution with hydrogen sulphide, and heating the resulting liquid with strong hydrochloric acid, it solidifies, on cooling, to a dazzling white mass of felted needles, consisting of the corresponding sulphur-compound, CH_2S.

Acetic Aldehyde, $C_2H_4O = CH_3 . COH = CH_3O . H$, generally designated by the simple name *aldehyde.*†—This substance is formed, among other products, when the vapor of ether or alcohol is transmitted through a red-hot tube; also, by the action of chlorine on weak alcohol, and by the other general reactions above mentioned. It is best prepared by the following process: 6 parts of oil of vitriol are mixed with 4 parts of rectified spirit of wine, and 4 parts of water; this mixture is poured upon 6 parts of powdered manganese dioxide contained in a capacious retort, in connection with a condenser cooled by ice-cold water; gentle heat is applied, and the process is interrupted when 6 parts of liquid have passed over. The distilled product is put into a small retort, with its own weight of calcium chloride, and redistilled; and this operation is repeated. The aldehyde, still retaining alcohol and other impurities, is mixed with twice its volume of ether, and saturated with dry ammoniacal gas; a crystalline compound of aldehyde and ammonia then separates, which may be washed with a little ether, and dried in the air. From this substance the aldehyde may be separated by distillation in a water-bath, with sulphuric acid diluted with an equal quantity of water; by careful rectification from calcium chloride, at a temperature not exceeding 30·5° C. (87° F.), it is obtained pure and anhydrous.

* Proceedings of the Royal Society, xvi. 156.

† Alcohol dehydrogenatus.

Aldehyde is a limpid, colorless liquid, of characteristic ethereal odor, which, when strong, is exceedingly suffocating. It has a density of 0·790, boils at 22° C. (72° F.), and mixes in all proportions with water, alcohol, and ether: it is neutral to test-paper, but acquires acidity on exposure to air, from the production of acetic acid: under the influence of platinum-black this change is very speedy. When a solution of this compound is heated with caustic potash, a remarkable brown resin-like substance is produced, the so-called *aldehyde-resin*. Gently heated with silver oxide, it reduces the latter without evolution of gas, the metal being deposited on the inner surface of the vessel as a brilliant and uniform film; the liquid contains silver acetate.

Aldehyde can be reconverted into alcohol by treating its aqueous solution with sodium amalgam, the liquid being kept slightly acid by repeated additions of hydrochloric acid.

When treated with hydrocyanic acid, aldehyde yields alanine (p. 616).

An aqueous solution of aldehyde, treated with hydrogen sulphide, yields an oily compound, $(C_2H_4O)_6 . SH_2$, which is resolved by acids into hydrogen sulphide and *sulphaldehyde*, C_2H_4S: the latter crystallizes in needles having an alliaceous odor.

Other reactions of aldehyde have been already mentioned.

Aldehyde-ammonia or *Ammonium aldehydate*, $C_2H_4O . NH_3$ or $C_2H_3(NH_4)O$, the formation of which has been already mentioned, forms transparent, colorless crystals, of great beauty: it has a mixed odor of ammonia and turpentine; it dissolves very easily in water, with less facility in alcohol, and with difficulty in ether; melts at about 76° C. (168° F.), and distils unchanged at 100°. Acids decompose it, with production of an ammoniacal salt and separation of aldehyde. Hydrogen sulphide converts it into a basic compound, $C_6H_{13}NS_2$, called *thialdine*. Sulphurous oxide gas is rapidly absorbed by a solution of aldehyde-ammonia, forming the crystalline compound $C_2H_3(NH_4)SO_3$, isomeric with taurin (p. 527). Aldehyde also combines with *acetic oxide*, forming the compound $C_2H_4O(C_2H_3O)_2O$; also with *ethyl oxide*, as will presently be further noticed.

Polymeric Modifications of Aldehyde.—When pure aldehyde is long preserved in a closely-stopped vessel, it is sometimes found to undergo spontaneous change into one, and even two isomeric modifications, differing completely in properties from the original compound. In a specimen kept some weeks at 0°, transparent acicular crystals were observed to form in considerable quantity, which, at a temperature little exceeding that of the freezing point of water, melted to a colorless liquid, miscible with water, alcohol, and ether; a few crystals remained, which sublimed without fusion, and were probably composed of the second substance. This new body, called *elaldehyde*, is identical in composition with aldehyde, but differs in properties and in the density of its vapor; the latter has a sp. gr. of 4·515, while that of aldehyde is only 1·532, or one-third of that number. It refuses to combine with ammonia, is not rendered brown by potash, and is but little affected by solution of silver.

The second modification, or *metaldehyde*, is sometimes produced in pure aldehyde kept at the common temperature of the air, even in hermetically sealed tubes; the conditions of its formation are unknown. It forms colorless, transparent, prismatic crystals, which sublime without fusion at a temperature above 100°, and are soluble in alcohol and ether, but not in water. They also were found, by analysis, to have the same composition as aldehyde.

Acetal.—When gaseous hydrochloric acid is passed into a solution of aldehyde in absolute alcohol, a compound of aldehyde and ethyl chloride, $C_2H_4O . C_2H_5Cl$, is produced, and this compound, treated with sodium

ethylate, forms a compound of aldehyde with ethyl oxide, called acetal:

$$\underset{\text{Ethylchloride of aldehyde.}}{C_2H_4O \cdot C_2H_5Cl} + \underset{\text{Sodium ethylate.}}{C_2H_5ONa} = NaCl + \underset{\text{Acetal.}}{C_2H_4O \cdot (C_2H_5)_2O}$$

This compound, which is isomeric with diethylic ethenate, $(C_2H_4)''(OC_2H_5)_2$ (p. 557), is likewise found among the products of the slow oxidation of alcohol under the influence of platinum-black.

To prepare it in this way, spirit of wine is poured into a large, tall, glass jar, to the depth of about an inch, and a shallow capsule, containing slightly moistened platinum-black, is arranged above the surface of the liquid; the jar is loosely covered by a glass plate, and left during two or three weeks in a warm situation. At the expiration of that time the liquid is found highly acid: it is to be neutralized with potassium carbonate, as much calcium chloride added as the liquid will dissolve, and the whole subjected to distillation, the first fourth only being collected. Fused calcium chloride added to the distilled product now throws up a light oily liquid, which is a mixture of acetal with alcohol, aldehyde, and acetic ether. By fresh treatment with calcium chloride, and long exposure to gentle heat in a retort, the aldehyde is expelled. The acetic ether is destroyed by caustic potash, and the alcohol removed by washing with water, after which the acetal is again digested with fused calcium chloride and redistilled.

Pure acetal is a thin, colorless liquid, of agreeable ethereal odor, of sp. gr. 0·821 at 22·2° C. (72° F.), and boiling at 140° C. (284° F.). It is soluble in 18 parts of water, and miscible in all proportions with alcohol and ether. It is unchanged in the air; but, under the influence of platinum-black, becomes converted into aldehyde, and eventually into acetic acid. Nitric and chromic acids produce a similar effect. Strong boiling solution of potash has no action on this substance.

Chloral, $C_2HCl_3O_2$. — This compound, already mentioned as being formed by the prolonged action of chlorine on absolute alcohol (p. 517), may be regarded as trichlorinated aldehyde. To prepare it, the current of chlorine must be kept up as long as hydrochloric acid gas continues to escape, and the product agitated with three times its volume of concentrated sulphuric acid. On gently warming this mixture in a water-bath, the impure chloral separates as an oily liquid, which floats on the surface of the acid; it is purified by distillation from fresh oil of vitriol, and afterward from a small quantity of quicklime, which must be kept completely covered by the liquid until the end of the operation. Chloral has also been obtained from starch, by distillation with hydrochloric acid and manganese dioxide.

Chloral is a thin, oily, colorless liquid, of peculiar and penetrating odor, which excites tears: it has but little taste. When dropped upon paper it leaves a greasy stain, which is not, however, permanent. It has a density of 1·502, and boils at 94° C. (201° F.). Chloral is freely soluble in water, alcohol, and ether; it forms, with a small quantity of water, a solid, crystalline hydrate; the solution is not affected by silver nitrate. Caustic baryta and lime decompose the vapor of chloral when heated in it, with appearance of ignition; the oxide is converted into chloride, carbon is deposited, and carbon monoxide set free. Solutions of caustic alkalies also decompose it, with production of a formate and chloroform.

When chloral is preserved for any length of time, even in a vessel hermetically sealed, it undergoes a very remarkable change — being converted into a solid, white, translucent substance, *insoluble chloral*, possessing the same composition as the liquid itself. This solid product is but very slightly soluble in water, alcohol, or ether; when exposed to heat, alone,

or in contact with oil of vitriol, it is reconverted into ordinary chloral. Solution of caustic potash resolves it into formic acid and chloroform.

Bromine acts upon alcohol in the same manner as chlorine, and gives rise to a product very similar in properties to the foregoing, called *bromal*, which contains C_2HBr_3O. It forms a crystallizable hydrate with water, and is decomposed by strong alkaline solutions into formic acid and *bromoform*.

The other aldehydes of the series $C_nH_{2n}O$ resemble acetic aldehyde in most of their reactions, especially in forming crystalline compounds with ammonia: this character distinguishes the fatty from the aromatic aldehydes, which react with ammonia in a different way. Another characteristic reaction of the fatty aldehydes is their conversion into amidated acids by the action of hydrocyanic acid (p. 685); in this manner amido-propionic acid, or alanine, $C_3H_7NO_2$, is formed from acetic aldehyde; amido-caproic acid, or leucine, $C_6H_{13}NO_2$, from valeral, $C_5H_{10}O_{11}$, &c. The fatty aldehydes are all converted into resinous compounds by the action of caustic potash.

All the known aldehydes of the fatty series are liquid at ordinary temperatures, and become more oily as their molecular weights increase. Their boiling points are given in the following table:

	Boiling point.			Boiling point.	
Acetic aldehyde	22° C.	72° F.	Œnanthylic aldehyde	152° C.	305° F.
Propionic "	55°–65° C.	131°–149° "	Caprylic "	178° "	352° "
Butyric "	68°–75° "	154°–167° "	Euodic "	213° "	329° "
Valeric "	93° "	199° "			

Euodic aldehyde is the essential constituent of oil of rue. It differs from the other compounds of the series by not reacting in the manner above mentioned with aniline.

Aldehyde belonging to the Series $C_nH_{2n-2}O$.

Acrylic Aldehyde, or Acrolein, $C_3H_4O = \begin{matrix} C(CH_2)''H \\ | \\ COH \end{matrix}$. — This compound is formed: — 1. By the oxidation of allyl alcohol, C_3H_6O. — 2. By the action of heat on the product of the union of acetone with bromine:

$$\underset{\text{Acetone.}}{CO(CH_3)_2} + Br_2 = \begin{matrix} C(CH_3)Br_2 \\ | \\ CH_2OH \end{matrix} = 2HBr + \underset{\text{Acrolein.}}{\begin{matrix} C(CH_2)''H \\ | \\ COH \end{matrix}}$$

3. By the dehydration of glycerin, when that substance is heated with phosphoric oxide, strong sulphuric acid, or acid potassium sulphate:

$$C_3H_8O_3 - 2OH_2 = C_3H_4O.$$

It is always produced in the destructive distillation of neutral fats containing glycerin, and is the cause of the intolerably pungent odor attending that process.

Pure acrolein is a thin, colorless, highly volatile liquid, lighter than water, and boiling at 52.2° C. (126° F.). Its vapor is irritating beyond description. It is sparingly soluble in water, freely in alcohol and ether.

Acrolein, by keeping, undergoes partial decomposition, yielding a white, flocculent, indifferent body, *disacryl;* the same substance is sometimes produced, together with acrylic acid, by exposure to the air. In contact with

alkalies, acrolein suffers violent decomposition, producing, like aldehyde, a resinous body. When exposed for some time in the air, or when mixed with silver oxide, it oxidizes with avidity, and passes into *acrylic acid*, $C_3H_4O_2$.

Aromatic Aldehydes, $C_nH_{2n-8}O$.

Benzoic Aldehyde, or **Bitter-almond Oil**, $C_7H_6O = C_6H_5.COH = C_7H_5O.H$. This compound is produced — 1. By the oxidation of amygdalin with nitric acid. — 2. By digesting bitter almonds with water for five or six hours at 30°–40° C. (86°–104° F.). The synaptase present then acts as a ferment on the amygdalin, converting it into glucose, benzoic aldehyde, and hydrocyanic acid (see page 579). Benzoic aldehyde is prepared by this process in large quantities, chiefly for use in perfumery. It does not pre-exist in the almonds, for the fat oil obtained from them by pressure is absolutely free from it. The crude oil has a yellow color, and contains a very considerable quantity of hydrocyanic acid: to free it from this impurity, it is agitated with dilute solution of ferrous chloride mixed with slaked lime in excess, and the whole is subjected to distillation; water passes over, accompanied by the purified essential oil, which is to be left for a short time in contact with a few fragments of fused calcium chloride to free it from water.

3. Benzoic aldehyde is formed, together with many other products, by the action of a mixture of manganese dioxide and sulphuric acid on albumin, fibrin, casein, and gelatin.

4. By the action of nascent hydrogen on chloride or cyanide of benzoyl:

$$C_7H_5OCl + H_2 = HCl + C_7H_6O.$$

Pure benzoic aldehyde is a thin, colorless liquid, of great refractive power, and peculiar, very agreeable odor: its density is 1·043, and its boiling point 180° C. (356° F.): it is soluble in about 30 parts of water, and miscible in all proportions with alcohol and ether. Exposed to the air, it greedily absorbs oxygen, and is converted into a mass of crystallized benzoic acid. Heated with solid *potassium hydrate*, it gives off hydrogen, and yields potassium benzoate. With the *alkaline bisulphites* it forms beautiful crystalline compounds. The vapor of the oil is inflammable, and burns with a bright flame and much smoke. It is very doubtful whether pure bitter-almond oil is poisonous; but the crude product, sometimes used for imparting an agreeable flavor to confectionery, is very dangerous.

Benzoic aldehyde, treated with *sodium amalgam*, is converted into benzyl alcohol, C_7H_8O. With *phosphorus pentachloride*, it yields benzylene chloride, $C_7H_6Cl_2$:

$$C_7H_6O + PCl_5 = PCl_3O + C_7H_6Cl_2.$$

Ammonia converts it into *hydrobenzamide*, a white crystalline neutral body, which, when boiled with aqueous potash, is converted into an isomeric basic compound, called *amarine:*

$$\underset{\text{Benzoic aldehyde.}}{3C_7H_6O} + 2NH_3 = \underset{\text{Hydrobenzamide.}}{(C_7H_6)''_3N_2} + 3OH_2.$$

All the aromatic aldehydes act with ammonia in a similar manner, and are thereby distinguished from the aldehydes of the fatty series.

Toluic Aldehyde, C_8H_8O, is produced by distilling a mixture of the calcium-salts of toluic and formic acids. The oily distillate agitated with acid

sodium sulphite, forms a crystalline compound, which, when distilled with sodium carbonate, yields the aldehyde, as an oil having a peppery odor, and boiling at 204° C. (399° F.). On exposure to the air, it is gradually converted into toluic acid, $C_8H_8O_2$. With alcoholic potash it forms potassium toluate and xylyl alcohol.

$$2C_8H_8O + KOH = C_8H_7KO_2 + C_8H_{10}O.$$

Cumic Aldehyde, $C_{10}H_{12}O$, exists together with cymene, $C_{10}H_{14}$, in the essential oil of cumin, and in that of water hemlock (*Cicuta virosa*), and may be obtained by agitating either of these oils with acid sodium sulphite, which takes up the cumic aldehyde, but not the cymene, and forms a crystalline compound, from which the aldehyde may be separated by distillation with potash. Cumic aldehyde is a colorless or slightly yellow liquid, having a powerful odor, and is easily oxidized in the air, so that it must be distilled in a current of carbonic acid gas. It is converted into cumic acid, $C_{10}H_{12}O_2$, by oxidation, and by alcoholic potash into potassium cumate and cymyl alcohol, $C_{10}H_{14}O$.

Sycocerylic Aldehyde, $C_{18}H_{28}O$, appears to be produced in thin prisms by oxidizing sycoceryl alcohol with aqueous chromic acid.

Cinnamic Aldehyde, C_9H_8O. — This compound, which is the only known member of the series of aldehydes $C_nH_{2n-10}O$, constitutes the essential part of the volatile oils of cinnamon and cassia, which are obtained from the bark of different trees of the genus *Cinnamonum*, order *Lauraceæ* — viz., oil of cinnamon, from Ceylon cinnamon, and oil of cassia, from Chinese cinnamon. The aldehyde may be separated from these oils by means of acid potassium sulphite. It is a colorless oil, rather heavier than water; may be distilled without alteration in a vacuum, or with de-aërated water: but absorbs oxygen quickly on exposure to the air, and passes into cinnamic acid. When fused with potash, it forms potassium cinnamate, and gives off hydrogen:

$$C_9H_8O + KOH = C_9H_7KO_2 + H_2.$$

Ammonia gas converts it into hydrocinnamide:

$$3C_9H_8O + 2NH_3 = (C_9H_8)'''_3N_2 + 3OH_2.$$

No aldehydes are known belonging to the series intermediate between $C_nH_{2n-2}O$, and $C_nH_{2n-8}O$.

There is indeed a well-known substance — viz., common camphor, or laurel camphor, having the composition $C_{10}H_{16}O$, which is that of the aldehyde of camphol, $C_{10}H_{18}O$ (p. 546); but its properties are not those of an aldehyde, inasmuch as it does not unite with alkaline bisulphites or with aniline, and when fused with potash, does not give off hydrogen and form the potassium-salt of the corresponding acid, but unites directly with the alkali, forming potassium campholate, $C_{10}H_{17}KO_2$. It may, however, be conveniently described in this place.

Camphor is obtained by distilling with water the wood of the camphor-tree (*Laurus Camphora*). When pure it forms a solid, white, crystalline and translucent mass, tough, and difficult to powder, and having a powerful and well-known odor. It melts when gently heated, and boils, distilling unchanged at a high temperature. It sublimes slowly at the temperature of the air, and often forms beautiful crystals on the sides of bottles or jars containing it exposed to the light. Camphor is very sparingly soluble in water, but readily soluble in alcohol, ether, and strong acetic acid. Small pieces of it thrown upon water revolve and move about on the surface, with more or less velocity in proportion to their smallness.

By the action of nitric acid aided by heat, camphor is gradually oxidized and dissolved, with production of *camphoric acid*, $C_{10}H_{16}O_2$ (p. 664).

Common camphor exerts a dextro-rotatory action on polarized light $[a] = +47{\cdot}4°$; but by distilling the essential oil of feverfew (*Pyrethrum parthenium*), and collecting apart the portion which passes over between 200° and 220° C. (392°–428° F.), an oil is obtained, which, on cooling, deposits a crystalline substance resembling common camphor in every respect, except that its action on polarized light is exactly equal and opposite: $[a] = -47{\cdot}4°$. The essential oils of many labiate plants, as rosemary, marjoram, lavender, and sage, often deposit a substance having the composition and all the properties of common camphor, excepting that it is inactive to polarized light.

Aldehydes derived from Diatomic Alcohols.

Diatomic alcohols can yield by oxidation two classes of aldehydes, accordingly as the substitution of O for H_2 takes place once or twice: the products thus formed may be distinguished as *first* and *second aldehydes*. Propene glycol, $C_3H_8O_2$, for example, might yield the two aldehydes, $C_3H_6O_2$ and $C_3H_4O_2$. Only a few of these compounds have, however, been obtained.

Of aldehydes derived from the glycols, C_nH_{2n+2}, only one is known, namely *glyoxal*, $C_2H_2O_2$, which is the second aldehyde of ordinary glycol, $C_2H_6O_2$. This compound is obtained, together with glyoxylic acid and other products, by the action of nitric acid upon alcohol. It may be separated by addition of a strong solution of acid sodium sulphite, with which it forms a crystalline compound: this compound, treated with barium chloride, yields the corresponding barium compound; and from this the glyoxal may be separated by dilute sulphuric acid. On evaporating the liquid, it is obtained as a transparent, amorphous, deliquescent mass, very soluble in water, alcohol, and ether. With an ammoniacal solution of *silver nitrate*, it forms a beautiful silver speculum. By a small quantity of *nitric acid* it is converted into glyoxylic acid, $C_2H_4O_4$; by a larger quantity, into oxalic acid, $C_2H_2O_4$. *Fixed caustic alkalies* and *alkaline earths* convert it into a salt of glycollic acid; *e g.*, $C_2H_2O_2 + KOH = C_2H_3KO_3$. A syrupy solution of glyoxal, heated with a strong aqueous solution of *ammonia*, yields two bases, *glyoxaline* and *glycosine*, according to the equations:

$$\underset{\text{Glyoxal.}}{2C_2H_2O_2} + 2NH_3 = \underset{\text{Glyoxaline.}}{C_3H_4N_2} + \underset{\text{Formic acid.}}{CH_2O_2} + 2OH_2$$

$$\underset{\text{Glyoxal.}}{3C_2H_2O_2} + 4NH_3 = \underset{\text{Glycosine.}}{C_6H_6N_4} + 6OH_2$$

Both these bases are crystalline: the glyoxaline is by far the more abundant of the two.

Of aldehydes derivable from diatomic alcohols belonging to other series, three only are known; viz., salicylic aldehyde, $C_7H_6O_2$, anisic aldehyde, $C_8H_8O_2$, and furfurol, $C_5H_4O_2$.

Salicylic Aldehyde, or **Salicylol**, $C_7H_6O_2 = C_6H_5O.COH$; also called *salicylous acid*, and *hydride of salicyl*. — This compound is produced by oxidizing the corresponding alcohol, saligenin, $C_7H_8O_2$, with potassium chromate and dilute sulphuric acid. As salicin (p. 581) is a glucoside of saligenin, and populin has the composition of benzoyl-salicin, salicylol may likewise be formed from these bodies by the action of oxidizing agents; it may be conveniently prepared by treating salicin or the concentrated extract of willow-bark with chromic acid. One part of salicin is dissolved in 10 parts of water, and mixed in a retort with 1 part of powdered potas-

sium bichromate and 2½ parts of oil of vitriol diluted with 10 parts of water; gentle heat is applied, and after the cessation of the effervescence first produced, the mixture is distilled. The yellow oily product is separated from the water, and purified by rectification from calcium chloride. Salicylol exists ready formed in the flowers of meadow-sweet (*Spiræa ulmaria*), and may be obtained, together with a terpene, by distilling the flowers with water. On neutralizing the distillate with potash, boiling to expel the hydrocarbon, slightly supersaturating the residue with phosphoric acid, and distilling, salicylol passes over, and may be purified by agitating the distillate with ether, treating the decanted ethereal solution with potash, supersaturating with phosphoric acid, and redistilling.

Salicylol is a thin, colorless, fragrant oil, acquiring a red tint by exposure to the air. It has a specific gravity of 1·173, solidifies at —20° C. (—4° F.), boils at 196·5° C. (385° F.), and burns when set on fire, with a bright smoky flame. Water dissolves a perceptible quantity of salicylol, acquiring its fragrant odor, and the property (likewise exhibited by salicylic acid) of producing a deep violet color with ferric salts. Alcohol and ether dissolve it in all proportions.

Salicylol is oxidized to salicylic acid by boiling with cupric oxide in alkaline solution, partially also by potassium bichromate and sulphuric acid; it likewise reduces silver oxide. When heated with potassium hydrate, it is converted into potassium salicylate, with evolution of hydrogen:

$$C_7H_6O_2 + KOH = C_7H_5KO_3 + H_2.$$

By nascent hydrogen it is converted into saligenin, $C_7H_8O_2$; by ammonia, into hydrosalicylamide:

$$\underset{\text{Salicylol.}}{3C_7H_6O_2} + 2NH_2 = 3OH_2 + \underset{\text{Hydrosalicyl-amide.}}{C_{21}H_{18}O_3N_2}$$

Salicylol decomposes alkaline carbonates, and dissolves in caustic alkalies, forming yellow crystallizable salts; the sodium-salt, for example, having the composition $C_7H_5NaO_2$. This salt and the corresponding potassium and ammonium-compounds, are soluble in water, and by treating their solutions with salts of barium, copper, lead, silver, &c., insoluble metallic derivatives of salicylol are precipitated. These compounds are commonly called *salicylites*, salicylol itself being called salicylous acid; but it is better to designate them as *sodium salicylol*, *copper salicylol*, &c., inasmuch as the metal contained in them does not appear to occupy the same place as in the salt of an ordinary acid, but rather to take the place of the alcoholic hydrogen in the molecule of salicylol, C_6H_5O . COH, so that sodium salicylol consists of C_6H_4NaO . COH. This salt, treated with methyl-iodide, yields sodium iodide and *methyl-salicylol*, $C_6H_4(CH_3)O$. COH, a compound exhibiting properties exactly analogous to those of salicylol itself. *Ethyl-salicylol*, $C_6H_4(C_2H_5)O$. COH, is obtained in a similar manner.* Ammonia acts upon these compounds in the same manner as on salicylol, converting them into methyl-hydrosalicylamide, $C_{21}H_{17}(CH_3)O_3N_2$, and ethyl-hydrosalicylamide, $C_{21}H_{17}(C_2H_5)O_3N_2$.

Salicylol is strongly attacked by *chlorine* and *bromine*, forming substitution-products, namely, chlorosalicylol, $C_7H_5ClO_2$, and bromo-salicylol, $C_7H_5BrO_2$, both of which are crystalline bodies possessing acid properties. *Iodine* dissolves in it, but does not form a substitution-product. Moderately strong *nitric acid* converts it into nitro-salicylol, $C_7H_5(NO_2)O_2$, which is also crystalline, and forms crystallizable salts. Chlorosalicylol is acted upon by ammonia in the same manner as salicylol, forming chlorohydrosalicylamide, or chlorosamide, $C_{21}H_{15}Cl_3O_3N_2$.

* *Perkin*, Chem. Soc. Journal [2], v. 418.

Methyl-salicylol and ethyl-salicylol are also attacked by chlorine and bromine, forming substitution-derivatives similar to those of salicylol itself, *e. g.*, ethyl-bromosalicylol, $C_7H_4(CH_3)BrO_2$.

Salicylol and all its substitution-derivatives above mentioned, form crystalline compounds with the acid sulphites of the alkali-metals.

Salicylol unites with *acetic oxide* or *anhydride*,* forming the crystalline compound $C_{11}H_{12}O_5 = C_7H_6O_2 . (C_2H_3O)_2O$. Acetic oxide likewise forms similar compounds with methyl- and ethyl-salicylol.

Sodium-salicylol, treated with acetic oxide, forms sodium acetate and *aceto-salicylol*.†

$$\underset{\text{Sodium-salicylol.}}{C_6H_4NaO . COH} + \underset{\substack{\text{Acetic}\\\text{oxide.}}}{(C_2H_3O)_2O} = \underset{\substack{\text{Sodium}\\\text{acetate.}}}{NaOC_2H_3O} + \underset{\text{Acetosalicylol.}}{C_6H_4(C_2H_3O)O . COH}$$

This compound has the same composition as coumaric acid, $C_9H_8O_3$, an acid produced by the hydration of coumarin, the odoriferous principle of the Tonka bean; but to obtain it by the reaction above mentioned, certain precautions are necessary. The acetic oxide must be added to powdered anhydrous sodium-salicylol suspended in pure dry ether, the reagents being employed in equivalent quantities; and after the whole has stood for twenty-four hours, the ethereal liquid must be filtered off from the sodium acetate, then evaporated, and the crystalline cake which separates on cooling, purified by pressure between bibulous paper, and crystallization from alcohol. Acetosalicylol thus prepared melts at 37° C. (98° F.), boils at about 258° C. (487° F.), and distils without decomposition. It is an aldehyde, like salicylol itself, and forms definite compounds with alkaline bisulphites. It is decomposed by alcoholic potash, with formation of potassium acetate and potassium-salicylol:

$$C_6H_4(C_2H_3O)O . COH + 2KOH = C_6H_4KO . COH + C_2H_3KO_2 + OH_2.$$

Acetosalicylol likewise unites directly with acetic oxide.

If the product of the action of acetic oxide on salicylol, instead of being treated in the manner above described, be poured into water after a few minutes' boiling, an oily liquid sinks to the bottom, and sodium-acetate remains in solution; and on distilling this oil, and collecting apart that which passes over after the temperature has risen to 290° C. (554° F.), a crystalline substance is obtained, having the composition of acetosalicylol minus one molecule of water: this substance is identical in every respect with natural *coumarin*, $C_9H_6O_2$. The dehydration of the acetosalicylol appears to be due to the action of the sodium-acetate, perhaps to the formation of an anhydroacetate or biacetate of sodium, $2C_2H_3NaO_2 . C_4H_6O_3$, analogous to potassium anhydrosulphate (p. 297), which appears to exert a more powerful dehydrating action than acetic oxide itself.

Coumarin thus obtained has lost the properties of an aldehyde, no longer uniting with alkaline bisulphites; it differs also from acetosalicylol in not being split up into acetic acid and salicylol by the action of strong potash, but simply taking up an atom of water and being converted into coumaric acid.

Coumarin, as already observed, is the odoriferous principle of the Tonka bean. It may be often seen, forming minute, colorless crystals under the skin of the seed, and between the cotyledons. It is best extracted by macerating the sliced beans in hot alcohol, and, after straining through cloth, distilling off the greater part of the spirit. The syrupy residue deposits, on standing, crystals of coumarin, which must be purified by pressure from a fat oil which abounds in the beans, and then crystallized from hot water.

* *Perkin*, Chem. Soc. Journal [2] v. 586.
† *Ibid.* [2], vi. 53, 181.

So obtained, coumarin forms slender, brilliant, colorless needles, fusible at about 67° C. (157° F.), boiling between 290° and 291° C. (555° F.), and distilling without decomposition at a higher temperature. It has a fragrant odor and burning taste; is very slightly soluble in cold water, more soluble in hot water, and in alcohol. It is unaffected by dilute acids or alkalies, which merely dissolve it. Boiling nitric acid converts it into picric acid, and a hot concentrated solution of potash converts it into *coumaric acid*, $C_9H_8O_3$, and eventually into salicylic acid. Coumarin exists in several other plants, as in *Melilotus officinalis*, *Asperula odorata*, and *Anthoxanthum odoratum*.

By acting on sodium salicylol with butyric and valeric oxides, Perkin has obtained homologues of coumarin, viz., butyric coumarin, $C_{11}H_{10}O_2$, and valeric coumarin, $C_{12}H_{12}O_2$.

Anisic Aldehyde, $C_8H_8O_2$, also called *Anisal* and *Hydride of Anisyl*, is formed, together with anisic acid, by oxidation of anisic alcohol, $C_8H_{10}O_2$, with platinum-black, or of anise oil with warm nitric acid:

$$\underset{\text{Anise oil.}}{C_{10}H_{12}O} + O_6 = \underset{\text{Anisic aldehyde.}}{C_8H_8O_2} + \underset{\text{Oxalic acid.}}{C_2H_2O_4} + OH_2.$$

It is a yellowish liquid, having an aromatic odor and a burning taste, nearly insoluble in water, but soluble in all proportions in alcohol and ether. It is converted by oxidation into anisic acid, $C_8H_8O_3$; by nascent hydrogen into anisic alcohol, $C_8H_{10}O_2$, and forms crystalline compounds with alkaline bisulphites. *Ammonia* converts it into anishydramide, $C_{24}H_{24}O_3N_2$. By *alcoholic potash* it is decomposed in the same manner as benzoic aldehyde, yielding potassium anisate and anisic alcohol:

$$\underset{\text{Anisic aldehyde.}}{2C_8H_8O_2} + KOH = \underset{\text{Potassium anisate.}}{C_8H_7KO_2} + \underset{\text{Anisic alcohol.}}{C_8H_{10}O}$$

Oil of anise is a solution of a solid substance called *anise-camphor*, having the composition $C_{10}H_{12}O$, in a fluid oil which appears to have the composition of oil of turpentine. The anise-camphor is so abundant as to cause the whole to solidify at 10° C. (50° F.). By pressure between folds of bibulous paper, and crystallization from alcohol, the camphor may be obtained pure. It forms colorless pearly plates, more fragrant than the crude oil, which melt when gently heated, and distil at a high temperature. This substance is attacked energetically by chlorine, bromine, and nitric acid: it combines with hydrochloric acid, but is unaffected by solution of caustic potash. With bromine the solid essence yields a white, inodorous, crystallizable compound, *bromanisal*, containing $C_{10}H_9Br_3O$. The action of chlorine is more complex, several successive compounds being produced. With sulphuric acid two products are obtained — a compound acid analogous to ethylsulphuric acid, and a white, solid, neutral substance, *anisoïn*, isomeric with the fluid essence.

The products of the action of nitric acid vary with the strength of the acid employed: the most important are, *anisic aldehyde; anisic acid; nitranisic acid*, a yellowish-white, crystalline, sparingly soluble powder; and *nitraniside*, a resinous body produced by fuming nitric acid.

Furfurol, $C_5H_4O_2$. —When sulphuric acid diluted with an equal bulk of water is carefully mixed with twice its weight of wheat-bran, and the adhesive pasty mass obtained is exposed in a proper vessel to the action of a current of steam, which is afterward condensed by a worm or refrigerator, a liquid is obtained which holds furfurol in solution. By redistillation several times repeated, the first half of the liquid only being collected, the

furfurol can be extracted from the water, and then by distillation alone obtained in a state of purity. The production of furfurol is very greatly increased, and the operation much facilitated, by previously depriving the bran of all starch, glutin, and soluble matter, by steeping it in cold dilute solution of caustic potash, and washing and drying by gentle heat or in the sun. Maceration in cold water for some time answers the same purpose, owing to the lactic acid formed in that case. Furfurol has a pale yellow color, and a fragrant odor like that of oil of cassia: its specific gravity is 1·165, and it boils at 162° C. (324° F.), distilling unchanged. It dissolves in all proportions in alcohol and to a very considerable extent in water, and is readily destroyed by strong acids and caustic alkalies, especially when aided by heat. The specific gravity of its vapor is 3·493. Furfurol may be converted into silver pyromucate by treating its aqueous solution with silver oxide:

$$2C_5H_4O_2 + 3Ag_2O = 2C_5H_3AgO_3 + 2Ag_2 + OH_2.$$

In contact with solution of ammonia, furfurol is converted in a few hours into *furfuramide*, $C_{15}H_{12}O_3N_2$, a yellowish-white, crystalline, insoluble substance, which is decomposed slowly by water, and instantly by an acid, into ammonia and furfurol. It may be crystallized from alcohol, however, in which it dissolves without change. When boiled with dilute potash, it is converted into the isomeric compound *furfurine*,* which is a base forming definite salts with acids.

Fucusol. — By treating several varieties of fucus with sulphuric acid in exactly the same manner as in the preparation of furfurol, Dr. Stenhouse obtained a series of substances, which he designates by the terms *fucusol*, *fucusamide*, and *fucusine*. They have exactly the same composition as the corresponding terms in the furfurol series, and also most of their properties, but differ in some details.

KETONES.

These bodies are derived from aldehydes by substitution of an alcohol-radical for hydrogen in the group COH; thus:

Acetic aldehyde	$CH_3.COH$
Acetic ketone or Acetone	$CH_3.COCH_3$.

They may be regarded as compounds of alcohol-radicals with acid radicals — acetone, for example, as methyl-acetyl; or as compounds of carbonyl, CO″, with two univalent alcohol-radicals, which may be either the same or different; *e. g.*:

$CO\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$	$CO\left\{\begin{matrix}CH_3\\C_3H_5\end{matrix}\right.$
Acetone or methyl-acetyl.	Methyl-propyl.

The only bodies of this class that have been carefully studied are those which correspond to the aldehydes $C_nH_{2n}O$, or to the fatty acids $C_nH_{2n}O_2$.

The names, formulæ, and boiling-points of the best known ketones of this series are given in the following table:

* See Organic Bases.

	Name.	Formula.	Boiling Point.
	Acetone, or Methyl-acetyl .	$CO(CH_3)(CH_3)$	56° C. 133° F.
	Ethyl-acetyl	$CO(CH_3)(CH_2CH_3)$ or $CO(CH_3)(C_2H_5)$	81° " 178° "
isomeric	Isopropyl-acetyl	$CO(CH_3)[CH(CH_3)_2]$	93·5° " 200° "
isomeric	Propyl-acetyl	$CO(CH_3)(CH_2C_2H_5)$ or $CO(CH_3)(C_3H_7)$	101° " 214° "
isomeric	Propione, or Ethyl-propyl .	$CO(C_2H_5)(C_2H_5)$	101° " 214° "
isomeric	Methyl-valeryl	$CO(C_4H_9)(CH_3)$	120° " 248° "
isomeric	Ethyl-butyryl	$CO(C_3H_7)(C_2H_5)$	128° " 262° "
isomeric	Isobutyl-acetyl	$CO(CH_3)[CH(C_2H_5)_2]$	138° " 280° "
isomeric	Butyrone, or Propyl-butyryl	$CO(C_3H_7)(C_3H_7)$	144° " 291° "

The ketones of this group, containing two equivalents of the same alcohol-radical, are produced:

1. By the action of carbon monoxide on sodium ethide and its homologues:

$$CO + 2NaC_nH_{2n+1} = Na_2 + CO(C_nH_{2n+1})_2.$$

For example:

$$\underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Sodium ethyl.}}{2NaC_2H_5} = Na_2 + \underset{\text{Propione.}}{CO(C_2H_5)_2}$$

2. By the action of zinc-methyl, and its homologues, on the acid chlorides, $C_nH_{2n-1}OCl$; *e. g.:*

$$\underset{\text{Zinc methide.}}{Zn(CH_3)_2} + \underset{\text{Acetic chloride.}}{2COCH_3Cl} = ZnCl_2 + \underset{\text{Acetone.}}{2CO(CH_3)_2}$$

3. By the oxidation of the secondary alcohols; thus:

$$\underset{\text{Isopropyl alcohol.}}{CH(CH_3)_2.OH} + O = OH_2 + \underset{\text{Acetone.}}{CO(CH_3)_2}$$

4. By the dry distillation of the calcium-salts of the fatty acids; *e. g.:*

$$\underset{\text{Calcium acetate.}}{Ca''\begin{cases}O(COCH_3)\\O(COCH_3)\end{cases}} = \underset{\text{Calcium carbonate.}}{COCa''O_2} + \underset{\text{Acetone.}}{CO(CH_3)_2}$$

The ketones formed in this manner from the successive members of the fatty acid series differ from one another by twice CH_2; thus:

Acetic acid . . .	$C_2H_4O_2$,	yields Acetone . . .	C_3H_6O.
Propionic acid . .	$C_3H_6O_2$,	" Propione . . .	$C_5H_{10}O$.
Butyric acid . .	$C_4H_8O_2$,	" Butyrone . . .	$C_7H_{14}O$.
Valeric acid . . .	$C_5H_{10}O_2$,	" Valerone . . .	$C_9H_{18}O$.

The intervals are filled up by ketones containing different alcohol-radicals; thus ethyl-acetyl, C_4H_8O, or $C_2H_5.COCH_3$, is intermediate between acetone and propione.

The ketones containing two different alcohol-radicals may be obtained by the second of the processes above given; *e. g.:*

$$\underset{\text{Acetic chloride.}}{2COCH_3Cl} + \underset{\text{Zinc ethyl.}}{Zn(C_2H_5)_2} = ZnCl_2 + \underset{\text{Ethyl acetyl.}}{2CO(CH_3)(C_2H_5)}$$

Or by distilling a mixture of the calcium-salts of two different fatty acids; thus:

$$\underset{\text{Valerate.}}{Ca(COC_4H_9)_2} + \underset{\text{Acetate.}}{Ca(COCH_3)_2} = 2CO_3Ca + \underset{\text{Butyl-acetyl.}}{2CO(CH_3)(C_4H_9)}$$

The formation of aldehydes by distilling a mixture of a formate with the salt of another fatty acid (p. 684), is a particular case of this last reaction.

Another mode of producing these compounds has been given by Frankland and Duppa,* depending on the consecutive action of sodium and the iodides of the alcohol-radicals C_nH_{2n+1}, on acetic ether; but we must be content with referring to it.

Every ketone is isomeric with an aldehyde belonging to the same series; thus acetone, $CH_3 . COCH_3$, is isomeric with propionic aldehyde, $C_2H_5 . COH$; butyrone, $C_3H_7 . COC_3H_7$, with œnanthylic aldehyde, $C_6H_{13} . COH$, &c. Formic acetone, $H . COH$, is identical with formic aldehyde.

Ketones resemble aldehydes in forming crystalline compounds with alkaline bisulphites, from which the ketone may be liberated by distillation with an alkali. They differ from the aldehydes: 1. In not being converted by oxidation into the corresponding acids. — 2. In being converted by nascent hydrogen into secondary alcohols, whereas the aldehydes are converted into primary alcohols. — 3. In not combining with aniline.

The only ketone that has been studied in detail is *acetone*, C_3H_6O, the ketone of acetic acid. This body is prepared, as already observed, by the destructive distillation of acetates, the calcium or the lead salt being the most convenient for the purpose. The crude distillate is saturated with potassium carbonate, and afterwards rectified in a water-bath from calcium chloride. Acetone may also be prepared by passing the vapor of strong acetic acid through an iron tube heated to dull redness, the acid being resolved into acetone, carbon dioxide, carbon monoxide, and carburetted hydrogen.

Acetone is also produced in the destructive distillation of citric acid, and may be procured from sugar, starch, and gum, by distillation with eight times their weight of powdered quicklime. The acetone is, in this case, accompanied by propione, which is an oily liquid, separable from the acetone by water, in which it is insoluble.

Pure acetone is a colorless limpid liquid, of peculiar odor: it has a density of 0·792, and boils at 55·5° C. (132° F.): the density of its vapor (referred to air) is 2·022. Acetone is very inflammable, and burns with a bright flame: it is miscible in all proportions with water, alcohol, and ether.

Nascent hydrogen converts it into isopropyl alcohol (p. 531); but at the same time a portion of the acetone doubles its molecule, and likewise takes up hydrogen, being thereby converted into a crystalline substance, *pinacone*, $C_6H_{14}O_2 = 2C_3H_6O + H_2$, which is perhaps a diatomic alcohol.

Acetone treated with *hydrocyanic acid*, water, and hydrochloric acid, is converted into *acetonic acid*, $C_4H_8O_3$, isomeric or identical with oxybutyric acid:

$$C_4H_6O + CNH + 2OH_2 + HCl = NH_4Cl + C_4H_8O_3.$$

When acetone is heated to 100° with *ammonia*, the two unite, with elimination of water, forming a basic compound, *acetonine*, related to acetone in the same manner as amarine (p. 690) to benzoic aldehyde:

$$\underset{\text{Acetone.}}{3C_3H_6O} + 2NH_3 = \underset{\text{Acetonine.}}{N_2(C_3H_6)''_3} + 3OH_2.$$

* Chem. Soc. Journal [2], v. 103.

Acetone distilled with *fuming sulphuric acid*, or other powerful dehydrating agents, is converted into *mesitylene*, $C_9H_{12} = 3C_3H_6O - OH_2$ (p. 499). *Phosphorus pentachloride* converts acetone into the compound, $C_3H_6Cl_2$, isomeric with propene chloride:

$$C_3H_6O + PCl_5 = PCl_3O + C_3H_6Cl_2.$$

This chloride differs in boiling point from propene chloride, but resembles the latter in its reaction with alcoholic potash, which converts it into chloropropene, C_3H_5Cl, identical with that obtained from propene.

Hydrochloric acid likewise converts acetone into a body composed of C_3H_5Cl, but isomeric, not identical, with the preceding. This compound, called *mesityl chloride*, is converted by alcoholic potash into *mesityl oxide*, $(C_3H_5)_2O$:

$$2C_3H_5Cl + 2KOH = 2KCl + OH_2 + (C_3H_5)_2O;$$

whereas chloropropene treated with alcoholic potash gives up hydrochloric acid, and yields allylene (p. 486): $C_3H_5Cl - HCl = C_3H_4$.

Of the aromatic ketones two only are known, viz., benzone and methyl-benzoyl.

Benzone or *Benzophenone*, $C_{13}H_{10}O$, or $C_6H_5 . COC_6H_5$, the ketone of benzoic acid, is produced by heating potassium benzoate; it is a crystalline body melting at 46° C. (115° F.), boiling at 315° C. (599° F.), and distilling without decomposition. Warm fuming nitric acid converts it into dinitrobenzone, $C_{13}H_8(NO_2)_2O$.

Methyl-benzoyl, $CH_3 . COC_6H_5$, is formed by distilling a mixture of calcium acetate and benzoate.

ORGANIC COMPOUNDS CONTAINING NITROGEN.

CYANOGEN COMPOUNDS.

We have already mentioned (p. 237) that the name cyanogen is applied to the univalent radical CN, derived from the saturated molecule $C^{iv}\left\{\begin{matrix}N'''\\H\end{matrix}\right.$, by abstraction of hydrogen. Cyanogen is a chlorous acid or negative radical, analogous to chlorine, bromine, and iodine: its compounds with metals and other positive radicals are called *cyanides:*

Hydrogen cyanide, or Hydrocyanic acid . .	$C\ N'''H$
Potassium cyanide	$C^{iv}N'''K$
Ethyl cyanide	$C^{iv}N'''C_2H_5$
Barium cyanide	$(C^{iv}N''')_2Ba''$
Ethene cyanide	$(C^{iv}N''')_2(C_2H_4)''$
Propenyl cyanide	$(C^{iv}N''')_3(C_3H_5)'''$

Cyanogen, in its capacity of a quasi-element, is often represented by the symbol Cy.

Cyanogen in the free state, C_2N_2, or $\begin{matrix}C\equiv N\\|\\C\equiv N\end{matrix}$, may be obtained by decomposing certain metallic cyanides. Pulverized and well-dried mercuric cyanide, $(CN)_2Hg''$, heated in a small retort of hard glass, undergoes decomposition, like the oxide under similar circumstances, yielding metallic mercury, a small quantity of a brown substance, of which mention will again be made, and cyanogen itself, a colorless, permanent gas, which must be collected over mercury. It has a pungent and very peculiar odor, remotely resembling that of peach-kernels, or hydrocyanic acid; exposed while at the temperature of 7·2° C. (45° F.) to a pressure of 3·6 atmospheres, it condenses to a thin, colorless, transparent liquid. Cyanogen is inflammable: it burns with a beautiful purple or peach-blossom-colored flame, generating carbon dioxide, and liberating nitrogen. The specific gravity of this gas is 1·806. Its composition may be demonstrated by mixing it with twice its measure of pure oxygen, and firing the mixture in the eudiometer; carbon dioxide is formed equal in volume to the oxygen employed, and a volume of nitrogen equal to that of the cyanogen is set free. Water dissolves 4 or 5 times its volume of cyanogen gas, and alcohol a much larger quantity: the solution rapidly decomposes, yielding ammonium-oxalate, $(C_2N_2+4OH_2 = C_2(NH_4)_2O_4)$, a brown insoluble matter, and other products.

Paracyanogen. — This is the brown or blackish substance above referred to, which is always formed in small quantity when cyanogen is prepared by heating mercuric cyanide, and probably, also, by the decomposition of solutions of cyanogen and of hydrocyanic acid. It is insoluble in water and alcohol, is dissipated by a very high temperature, and contains, according to Johnston, carbon and nitrogen in the same proportion as cyanogen.

Hydrogen Cyanide; Hydrocyanic or Prussic Acid, HCy.—This very important compound, so very remarkable for its poisonous properties, was discovered as early as 1782 by Scheele. It may be formulated as *azomethane*, $C^{IV}\left\{\begin{matrix} N''' \\ H \end{matrix}\right.$; that is to say, methane or marsh-gas having three of its hydrogen-atoms replaced by nitrogen, or as *methenyl nitrile*, $(CH)'''N$, that is, ammonia in which the three atoms of hydrogen are replaced by the trivalent radical methenyl.

Hydrocyanic acid may be prepared in a state of purity, and anhydrous, by the following process: A long glass tube, filled with dry mercuric cyanide, is connected by one extremity with an arrangement for furnishing dry sulphuretted hydrogen gas, while a narrow tube attached to the other end is made to pass into a narrow-necked phial plunged into a freezing mixture. Gentle heat is applied to the tube, the contents of which suffer decomposition in contact with the gas, mercuric sulphide and hydrogen cyanide being produced: the latter is condensed in the receiver to the liquid form. A little of the mercuric cyanide should be left undecomposed, to avoid contamination of the product with sulphuretted hydrogen. The pure acid is a thin, colorless, and exceedingly volatile liquid, which has a density of 0·7058 at 7·2° C. (45° F.), boils at 26·1° C. (79° F.), and solidifies, when cooled, to —18° C. (—0·4° F.); its odor is very powerful and most characteristic, much resembling that of peach-blossoms or bitter-almond oil; it has a very feeble acid reaction, and mixes with water and alcohol in all proportions. In the anhydrous state this substance constitutes one of the most formidable poisons known, and even when largely diluted with water, its effects upon the animal system are exceedingly energetic: it is employed, however, in medicine, in very small doses. The inhalation of the vapor should be carefully avoided in all experiments in which hydrocyanic acid is concerned, as it produces headache, giddiness, and other disagreeable symptoms: ammonia and chlorine are the best antidotes.

The acid in its pure form can scarcely be preserved: even when enclosed in a carefully stopped bottle, it is observed after a very short time to darken, and eventually to deposit a black substance containing carbon, nitrogen, and perhaps hydrogen: ammonia is formed at the same time, and many other products. Light favors this decomposition. Even in a dilute condition it is apt to decompose, becoming brown and turbid, but not always with the same facility, some samples resisting change for a great length of time, and then suddenly solidifying to a brown, pasty mass in a few weeks.

When hydrocyanic acid is mixed with concentrated mineral acids, hydrochloric acid, for example, the whole solidifies to a crystalline paste of sal-ammoniac and formic acid:

$$CNH + 2H_2O = NH_3 + CH_2O_2.$$

On the other hand, when dry ammonium formate is heated to 200°, it is almost entirely converted into hydrocyanic acid and water.

Aqueous solution of hydrocyanic acid may be prepared by various means. The most economical, and by far the best, where considerable quantities are wanted, is to decompose yellow potassium ferrocyanide at boiling heat with dilute sulphuric acid. For example, 500 grains of the powdered ferrocyanide may be dissolved in four or five ounces of warm water, and introduced into a capacious flask or globe, connected by a perforated cork and wide bent tube with a Liebig's condenser well supplied with cold water; 300 grains of oil of vitriol are diluted with three or four times as much water and added to the contents of the flask; and the distillation is carried on till about half the liquid has distilled over, after which the process may be interrupted. The residue in the retort is a white or yellow

mass, consisting of potassio-ferrous ferrocyanide (see p. 707), mixed with potassium sulphate:

$2K_4Fe''Cy_6$	+	$3SO_4H_2$	=	$6HCy$	+	$K_2Fe''_2Cy_6$	+	$3SO_4K_2$
Potassium ferrocyanide.		Hydrogen sulphate.		Hydrogen cyanide.		Potassio-ferrous ferrocyanide.		Potassium sulphate.

When hydrocyanic acid is wanted for the purposes of pharmacy, it is best to prepare a strong solution in the manner above described, and then, having ascertained its exact strength, to dilute it with pure water to the standard of the Pharmacopœia, viz., 2 per cent. of real acid. This examination is best made by precipitating with excess of silver nitrate a known weight of the acid to be tried, collecting the insoluble silver cyanide upon a small filter previously weighed, washing, drying, and lastly reweighing the whole. From the weight of the cyanide that of the hydrocyanic acid can be easily calculated, a molecule of the one (CNAg=134) corresponding to a molecule of the other (CNH=27); or the weight of the silver cyanide may be divided by 5, which will give a close approximation to the truth.

Another very good method for determining the amount of hydrocyanic acid in a liquid has been suggested by Liebig. It is based upon the property possessed by potassium cyanide of dissolving a quantity of silver cyanide sufficient to produce with it a double cyanide containing equivalent quantities of silver cyanide and potassium cyanide (KCy . AgCy). Hence a solution of hydrocyanic acid, which is supersaturated with potash, and mixed with a few drops of solution of common salt, will not yield a permanent precipitate with silver nitrate before the whole of the hydrocyanic acid is converted into the above double salt. If we know the amount of silver in a given volume of the nitrate solution, it is easy to calculate the quantity of hydrocyanic acid: for this quantity will stand to the amount of silver in the nitrate consumed, as 2 molecules of hydrocyanic acid to 1 atom of silver, *i. e.*:

$$108 : 54 = \text{silver consumed} : x.$$

It is a common remark, that the hydrocyanic acid made from potassium ferrocyanide keeps better than that made by other means. The cause of this is ascribed to the presence of a trace of mineral acid. Everitt found that a few drops of hydrochloric acid, added to a large bulk of the pure dilute acid, preserved it from decomposition, while another portion, not so treated, became completely spoiled.

A very convenient process for the extemporaneous preparation of an acid of definite strength, is to decompose a known quantity of potassium cyanide with solution of tartaric acid: 100 grains of crystallized tartaric acid in powder, 44 grains of potassium cyanide, and 2 measured ounces of distilled water, shaken up in a phial for a few seconds, and then left at rest, in order that the precipitate may subside, will yield an acid of very nearly the required strength. A little alcohol may be added to complete the separation of the cream of tartar: no filtration or other treatment need be employed.

The production of hydrocyanic acid from bitter almonds has been already mentioned in connection with the history of this volatile oil. Bitter almonds, the kernels of plums and peaches, the seeds of the apple, the leaves of the cherry-laurel, and various other parts of plants belonging to the great natural order *Rosaceæ*, yield on distillation with water a sweet-smelling liquid containing hydrocyanic acid. This is probably due in all cases to the decomposition of amygdalin under the influence of emulsin or synaptase present in the organic structure (p. 579). Hydrocyanic acid exists ready formed to a considerable extent in the juice of the bitter cassava.

The presence of hydrocyanic acid is detected with the utmost ease: its remarkable odor and high degree of volatility almost sufficiently characterize it. With solution of silver nitrate it gives a dense curdy white precipitate, much resembling the chloride, but differing from that substance in not blackening so readily by light, in being soluble in boiling nitric acid, and in suffering complete decomposition when heated in the dry state, metallic silver being left: the chloride under the same circumstances merely fuses, but undergoes no chemical change. The production of Prussian blue by "Scheele's test" is an excellent and most decisive experiment, which may be made with a very small quantity of the acid. The liquid to be examined is mixed with a few drops of solution of ferrous sulphate and an excess of caustic potash, and the whole exposed to the air for 10 or 15 minutes, with agitation, whereby the ferrous salt is partly converted into ferric salt: hydrochloric acid is then added in excess, which dissolves the iron oxide, and, if hydrocyanic acid be present, leaves Prussian blue as an insoluble powder. The reaction will be explained in connection with the ferrocyanides (p. 707).

Another very delicate test for hydrocyanic acid will be mentioned in connection with sulphocyanic acid.

Metallic Cyanides. — The most important of the metallic cyanides are the following: they bear the most perfect analogy to the haloïd salts.

Potassium Cyanide, CNK or KCy. — Potassium heated in cyanogen gas, takes fire and burns in a very beautiful manner, yielding potassium cyanide: the same substance is produced when potassium is heated in the vapor of hydrocyanic acid, hydrogen being liberated. When pure nitrogen gas is transmitted through a white-hot tube containing a mixture of potassium carbonate and charcoal, a small quantity of potassium cyanide is formed, which settles on the cooler portions of the tube as a white amorphous powder: carbon monoxide is at the same time evolved.* If azotized organic matter of any kind, capable of furnishing ammonia by destructive distillation, as horn-shavings, parings of hides, &c., be heated to redness with potassium carbonate in a close vessel, a very abundant production of potassium cyanide results, which cannot, however, be advantageously extracted by direct means, but in practice is always converted into ferrocyanide, which is a much more stable substance, and crystallizes better.

There are several methods by which potassium cyanide may be prepared for use. It may be made by passing the vapor of hydrocyanic acid into a cold alcoholic solution of potash: the salt is then deposited in the crystalline form, and may be separated from the liquid, pressed, and dried. Potassium ferrocyanide, heated to whiteness in a nearly close vessel, evolves nitrogen and other gases, and leaves a mixture of carbon, iron carbide, and potassium cyanide, which latter salt is not decomposed unless the temperature is excessively high. Mr. Donovan recommends the use in this process of a wrought-iron mercury-bottle, which is to be half filled with the ferrocyanide, and arranged in a good air-furnace capable of giving the requisite degree of heat; a bent iron tube is fitted to the mouth of the bottle and made to dip half an inch into a vessel of water: this serves to give exit to the gas. The bottle is gently heated at first, but the temperature is ultimately raised to whiteness. When no more gas issues, the tube is stopped with a cork, and, when the whole is quite cold, the bottle is cut asunder in the middle by means of a chisel and sledge-hammer, and the pure white fused salt carefully separated from the black spongy mass

* According to recent experiments by MM. Margueritte and de Sourdeval, the formation of cyanide appears to be more abundant if the potash be replaced by baryta. If the barium cyanide thus formed be exposed to a stream of superheated steam at 300° C., the nitrogen of the salt is eliminated in the form of ammonia. Margueritte and de Sourdeval recommend this process as a method of preparing ammonia by means of atmospheric nitrogen.

below, and preserved in a well-stopped bottle: the black substance contains much cyanide, which may be extracted by a little cold water. It would be better, perhaps, in the foregoing process, to deprive the potassium ferrocyanide of its water of crystallization before introducing it into the iron vessel.

Liebig has published a very easy and excellent process for making potassium cyanide, which does not, however, yield it pure, but mixed with potassium cyanate. For most of the applications of potassium cyanide, electro-plating and gilding, for example, for which a considerable quantity is now required, this impurity is of no consequence. Eight parts of potassium ferrocyanide are rendered anhydrous by gentle heat, and intimately mixed with 3 parts of dry potassium carbonate: this mixture is thrown into a red-hot earthen crucible and kept in fusion, with occasional stirring, until gas ceases to be evolved, and the fluid portion of the mass becomes colorless. The crucible is left at rest for a moment, and then the clear salt decanted from the heavy black sediment at the bottom, which is principally metallic iron in a state of minute division. The reaction is represented by the equation:

$$\underset{\text{Ferrocyanide.}}{K_4Fe''Cy_6} + \underset{\text{Carbonate.}}{CO_3K_2} = \underset{\text{Cyanide.}}{5KCy} + \underset{\text{Cyanate.}}{CyKO} + Fe + CO_2.$$

The product may be advantageously used, instead of potassium ferrocyanide, in the preparation of hydrocyanic acid, by distillation with diluted oil of vitriol.

Potassium cyanide forms colorless, cubic or octohedral crystals, deliquescent in the air, and exceedingly soluble in water: it dissolves in boiling alcohol, but separates in great measure on cooling. It is readily fusible, and undergoes no change at a moderate red or even white heat, when excluded from air; otherwise, oxygen is absorbed and the cyanide becomes cyanate. Its solution always has an alkaline reaction, and when exposed to the air exhales the odor of hydrocyanic acid: it is decomposed by the feeblest acids, even the carbonic acid of the atmosphere, and when boiled in a retort is slowly converted into potassium formate, with separation of ammonia. This salt is anhydrous: it is said to be as poisonous as hydrocyanic acid itself.

Potassium cyanide has been derived from a curious and unexpected source. In some of the iron furnaces in Scotland, where raw coal is used for fuel with the hot blast, a saline-looking substance is occasionally observed to issue in a fused state from the tuyere-holes of the furnace, and concrete on the outside. This proved, on examination by Dr. Clark, to be principally potassium cyanide.

Sodium Cyanide, NaCy, is a very soluble salt, corresponding closely with the foregoing, and obtained by similar means.

Ammonium Cyanide, NH_4Cy. — This is a colorless, crystallizable, and very volatile substance, prepared by distilling a mixture of potassium cyanide and sal-ammoniac; or by mingling the vapor of anhydrous hydrocyanic acid with ammoniacal gas; or, lastly, according to the observations of M. Langlois, by passing ammonia over red-hot charcoal. It is very soluble in water, subject to spontaneous decomposition, and is slightly poisonous.

Mercuric Cyanide, $(CN)_2Hg''$, or $Hg''Cy_2$.—One of the most remarkable properties of cyanogen is its powerful attraction for certain of the less oxidable metals, as silver, and more particularly for mercury and palladium. Dilute hydrocyanic acid dissolves finely-powdered mercuric oxide with the utmost ease: the liquid loses all odor, and yields on evaporation crystals of mercuric cyanide. Potassium cyanide is in like manner decomposed by mercuric oxide, potassium hydrate being produced. Mer-

curic cyanide is generally prepared from common potassium ferrocyanide; 2 parts of the salt are dissolved in 15 parts of hot water, and 3 parts of dry mercuric sulphate are added; the whole is boiled for fifteen minutes, and filtered hot from the iron oxide, which separates. The solution, on cooling, deposits the mercuric cyanide in crystals. Mercuric cyanide forms white, translucent prisms, much resembling those of corrosive sublimate: it is soluble in 8 parts of cold water, and in a much smaller quantity at a higher temperature, and also in alcohol. The solution has a disagreeable metallic taste, is very poisonous, and is not precipitated by alkalies. Mercuric cyanide is used in the laboratory as a source of cyanogen.

Silver Cyanide, AgCy, has been already described. — *Zinc cyanide*, $ZnCy_2$, is a white insoluble powder, prepared by mixing zinc acetate with hydrocyanic acid. — *Cobalt cyanide*, $CoCy_2$, is obtained by similar means: it is dirty-white, and insoluble. — *Palladium cyanide*, $PdCy_2$, forms a yellowish-white precipitate when the chloride of that metal is mixed with a soluble cyanide, including that of mercury. — *Auric cyanide*, $AuCy_3$, is yellowish-white and insoluble, but freely dissolved by solution of potassium cyanide.

Iron Cyanides.—These compounds are scarcely known in the separate state, on account of their great tendency to form double salts. On adding potassium cyanide to a ferrous salt, a yellowish-red flocculent precipitate is formed, consisting chiefly of ferrous cyanide, $FeCy_2$, but always containing a certain quantity of potassium cyanide, and dissolved as ferrocyanide by excess of that salt. Ferric cyanide, Fe_2Cy_6, is known only in solution. Pelouze obtained an insoluble green compound containing Fe_3Cy_8, or $FeCy_2 . Fe_2Cy_6$, by passing chlorine gas into a boiling solution of potassium ferrocyanide.

The iron cyanides unite with other metallic cyanides, forming two very important groups of compounds, called *ferrocyanides* and *ferricyanides*, the composition of which may be illustrated by the respective potassium-salts:

Ferrocyanide, $K_4Fe''Cy_6$, or $4KCy . Fe''Cy_2$.
Ferricyanide, $K_3Fe'''Cy_6$, or $3KCy . Fe'''Cy_3$.*

It will be seen from these formulæ, that the ferro- and ferricyanides differ from one another only by one atom of univalent metal, and, accordingly, it is found that the former may be converted into the latter, by the action of oxidizing (metal-abstracting) agents, and the latter into the former by the action of reducing (metal-adding) agents. Thus potassium ferrocyanide is easily converted into the ferricyanide by the action of chlorine, and many double ferrocyanides may be formed from ferricyanides by the action of alkalies in presence of a reducing agent; thus potassium ferricyanide, $K_3Fe'''Cy_6$, is easily converted into ammonio-tripotassic ferrocyanide, $(NH_4)K_3Fe''Cy_6$, by the action of ammonia in presence of glucose.†

* Strictly speaking, the formula of potassium ferricyanide should be $6KCy . Fe'''_2Cy_6$ (see Iron, p. 398); but, for comparing the composition of the ferricyanides with that of the ferrocyanides, the simpler formula above given is more convenient.

† The ferrocyanides and ferricyanides are sometimes regarded as salts of peculiar compound radicals containing iron, viz., *ferrocyanogen*, $Fe''Cy_6$, and *ferricyanogen*, $Fe'''Cy_6$, the first being quadrivalent, the second trivalent; but there is nothing gained by this assumption. For a discussion of the formulæ of these salts, and of the double cyanides in general, see Watts's Dictionary of Chemistry, vol. ii. p. 201.

Ferrocyanides.

Potassium Ferrocyanide, $K_4Fe''Cy_6$, or $4KCy . Fe''Cy_2$, commonly called *yellow prussiate of potash.* — This important salt is formed: — 1. By digesting precipitated ferrous cyanide in aqueous solution of potassium cyanide. — 2. By digesting ferrous hydrate with potassium cyanide, potash being formed at the same time:

$$6KCy + Fe''H_2O_2 = 2KHO + K_4Fe''Cy_6.$$

3. Ferrous cyanide with aqueous potash:

$$3Fe''Cy_2 + 4KHO = 2Fe''H_2O_2 + K_4Fe''Cy_6.$$

4. Aqueous potassium cyanide with metallic iron: if the air be excluded, hydrogen is evolved:

$$6KCy + Fe + 2OH_2 = K_4Fe''Cy_6 + 2KHO + H_2;$$

but if the air has access to the liquid, oxygen is absorbed, and no hydrogen is evolved:

$$6KCy + Fe + OH_2 + O = K_4Fe''Cy_6 + 2KHO.$$

5. Ferrous sulphide with aqueous potassium cyanide:

$$6KCy + Fe''S = K_2S + K_4Fe''Cy_6.$$

6. Any soluble ferrous salt with potassium cyanide; *e. g.:*

$$6KCy + SO_4Fe'' = SO_4K_2 + K_4Fe''Cy_6.$$

Potassium ferrocyanide is manufactured on the large scale by the following process: — Dry refuse animal matter of any kind is fused at a red heat with impure potassium carbonate and iron filings, in a large iron vessel, from which the air should be excluded as much as possible; potassium cyanide is generated in large quantity. The melted mass is afterwards treated with hot water, which dissolves out the cyanide and other salts, the cyanide being quickly converted by the oxide or sulphide * of iron into ferrocyanide. The filtered solution is evaporated, and the first-formed crystals are purified by re-solution. If a sufficient quantity of iron be not present, great loss is incurred by the decomposition of the cyanide into potassium carbonate and ammonia.

A new process for the preparation of potassium ferrocyanide has lately been proposed by M. Gélis. It consists in converting carbon bisulphide into ammonium sulphocarbonate by agitating it with ammonium sulphide: $CS_2 + (NH_4)_2S = (NH_4)_2CS_3$, and heating the product thus obtained with potassium sulphide, whereby potassium sulphocyanate (p 717) is formed, with evolution of ammonium sulphide and hydrogen sulphide:

$$2(NH_4)_2CS_3 + K_2S = 2CNSK + 2(NH_4)HS + 3H_2S.$$

The potassium sulphocyanate is dried, mixed with finely divided metallic iron, and heated for a short time in a closed iron vessel to dull redness, whereby the mixture is converted into potassium ferrocyanide, potassium sulphide, and iron sulphide:

$$6CNSK + Fe_6 = K_4Fe''Cy_6 + 5Fe''S + K_2S.$$

By treatment with water, the sulphide and ferrocyanide of potassium are dissolved, and on evaporation the ferrocyanide is obtained in crystals. It remains to be seen whether this ingenious process is capable of being carried out upon a large scale.

* The sulphur is derived from the reduced sulphate of the crude pearl-ashes and the animal substances used in the manufacture.

Potassium ferrocyanide forms large, transparent, yellow crystals, $K_4Fe''Cy_6 . 3$ Aq., derived from an octohedron with a square base: they cleave with facility in a direction parallel to the base of the octohedron, and are tough and difficult to powder. They dissolve in 4 parts of cold and 2 parts of boiling water, and are insoluble in alcohol. They are permanent in the air, and have a mild saline taste. The salt has no poisonous properties, and, in small doses at least, is merely purgative. Exposed to a gentle heat, it loses 3 molecules of water, and becomes anhydrous: at a high temperature it yields potassium cyanide, iron carbide, and various gaseous products; if air be admitted, the cyanide becomes cyanate.

Potassium ferrocyanide is a chemical reagent of great value; when mixed in solution with neutral or slightly acid salts of the heavy metals, it gives rise to precipitates which very frequently present highly characteristic colors. In most of these compounds the potassium is simply displaced by the new metal: the beautiful brown ferrocyanide of copper contains, for example, $Cu''_2Fe''Cy_6$, or $2Cu''Cy_2 . Fe''Cy_2$, and that of lead, $Pb''_2Fe''Cy_6$.

With *ferrous salts*, potassium ferrocyanide gives a precipitate which is perfectly white, if the air be excluded and the solution is quite free from ferric salt, but quickly turns blue on exposure to the air. It consists of *potassio-ferrous ferrocyanide*, $K_2Fe''_2Cy_6$, or potassium ferrocyanide having half the potassium replaced by iron. The same salt is produced in the preparation of hydrocyanic acid by distilling potassium ferrocyanide with dilute sulphuric acid (p. 701).

When a soluble ferrocyanide is added to the solution of a *ferric salt*, a deep blue precipitate is formed, consisting of *ferric ferrocyanide*, Fe_7Cy_{18}, or $Fe'''_4Fe''_3Cy_{18}$, or $4Fe'''Cy_3 . 3Fe''Cy_2$, which in combination with 18 molecules of water constitutes ordinary Prussian blue. This beautiful pigment is best prepared by adding potassium ferrocyanide to ferric nitrate or chloride:

$$3K_4Fe''Cy_6 + 2Fe'''_2Cl_6 = 12KCl + Fe_7Cy_{18}.$$

It is also formed by precipitating a mixture of ferrous and ferric salts with potassium cyanide:

$$18KCy + 3Fe''Cl_2 + 2Fe'''_2Cl_6 = 18KCl + Fe_7Cy_{18}.$$

This reaction explains Scheele's test for prussic acid (p. 703). Prussian blue is also formed by the action of air, chlorine-water, and other oxidizing agents, on potassio-ferrous ferrocyanide; probably thus:

$$6K_2Fe''_2Cy_6 + O_3 = Fe_7Cy_{18} + 3K_4Fe''Cy_6 + Fe_2O_3.$$

It is chiefly by this last reaction that Prussian blue is prepared on the large scale, potassium ferrocyanide being first precipitated by ferrous sulphate, and the resulting white or light blue precipitate either left to oxidize by contact with the air, or subjected to the action of nitric acid, chlorine, hypochlorites, chromic acid, &c. The product, however, is not pure ferric ferrocyanide: for it is certain that another and simpler reaction takes place at the same time, by which the potassio-ferrous ferrocyanide, $(K_2Fe'')Fe''Cy_6$, is converted, by abstraction of an atom of potassium, into *potassio-ferrous ferricyanide*, $(KFe'')Fe'''Cy_6$, which also possesses a fine deep-blue color. Commercial Prussian blue is, therefore, generally a mixture of this compound with ferric ferrocyanide, $Fe'''_4Fe''_3Cy_{18}$, the one or the other predominating according to the manner in which the process is conducted.

Prussian blue in the moist state forms a bulky precipitate, which shrinks to a comparatively small compass when well washed and dried by a gentle heat. In the dry state it is hard and brittle, much resembling in appear-

ance the best indigo: the freshly fractured surfaces have a beautiful copper-red lustre, similar to that produced by rubbing indigo with a hard body. Prussian blue is quite insoluble in water and dilute acids, with the exception of oxalic acid, in a solution of which it dissolves, forming a deep-blue liquid, which is sometimes used as ink: concentrated oil of vitriol converts it into a white, pasty mass, which again becomes blue on addition of water. Alkalies destroy the color instantly: they dissolve out a ferrocyanide, and leave ferric oxide. Boiled with water and mercuric oxide, it yields a cyanide of the metal, and ferric oxide. Heated in the air, Prussian blue burns like tinder, leaving a residue of ferric oxide. Exposed to a high temperature in a close vessel, it gives off water, ammonium cyanide, and ammonium carbonate, and leaves carbide of iron. It forms a very beautiful pigment, both as oil and water color, but has little permanency.

Common or basic Prussian blue is an inferior article prepared by precipitating a mixture of ferrous sulphate and alum with potassium ferrocyanide, and exposing the precipitate to the air. It contains alumina, which impairs the color, but adds to the weight.

Soluble Prussian blue is obtained by adding ferric chloride to an excess of potassium ferrocyanide; it is insoluble in the saline liquor, but soluble in pure water. It has a deep blue color, and probably consists of potassio-ferrous ferricyanide.

Hydrogen Ferrocyanide or Hydroferrocyanic Acid, $H_4Fe''Cy_6$, discovered by Mr. Porrett, is prepared by decomposing ferrocyanide of lead or copper suspended in water by a stream of sulphuretted hydrogen gas. The filtered solution evaporated in a vacuum over oil of vitriol, yields the acid in the solid form. If the aqueous solution be agitated with ether, nearly the whole of the acid separates in colorless, crystalline laminæ; it may even be made in large quantity by adding hydrochloric acid to a strong solution of potassium ferrocyanide in water free from air, and shaking the whole with ether. The crystals may be dissolved in alcohol, and the acid again thrown down by ether. Hydroferrocyanic acid differs completely from hydrocyanic acid: its solution in water has a powerfully acid taste and reaction, and decomposes alkaline carbonates with effervescence: it does not dissolve mercuric oxide in the cold, but when heat is applied, undergoes decomposition, forming mercuric cyanide and ferrous cyanide: $H_4Fe''Cy_6 + 2Hg''O = 2Hg''Cy_2 + Fe''Cy_2 + 2OH_2$; but the ferrous cyanide is immediately oxidized by the excess of mercuric oxide, with separation of metallic mercury. In the dry state the acid is very permanent, but when long exposed to the air in contact with water, it is entirely converted into Prussian blue.

Sodium ferrocyanide, $Na''Fe''Cy_6 . 12$ Aq., crystallizes in yellow four-sided prisms, which are efflorescent in the air and very soluble.

Ammonium ferrocyanide, $(NH_4)''Fe''Cy_6 . 3$ Aq., is isomorphous with potassium ferrocyanide: it is easy soluble, and is decomposed by ebullition. *Barium ferrocyanide*, $Ba''_2Fe''Cy_6$, prepared by boiling potassium ferrocyanide with a large excess of barium chloride, or Prussian blue with baryta-water, forms minute yellow, anhydrous crystals, which have but a small degree of solubility even in boiling water. The corresponding compounds of *strontium*, *calcium*, and *magnesium* are more freely soluble. The ferrocyanides of *silver*, *lead*, *zinc*, *manganese*, and *bismuth* are white and insoluble; those of *nickel* and *cobalt* are pale-green and insoluble; and, lastly, that of *copper* has a beautiful reddish-brown tint.

There are also several double ferrocyanides. When, for example, concentrated solutions of calcium chloride and potassium ferrocyanide are mixed, a sparingly soluble crystalline precipitate falls, containing $K_2Ca''Fe''Cy_6$.

Ferricyanides.

These salts are formed, as already observed, by abstraction of metal from the ferrocyanides; in other words, by the action of oxidizing agents.

Potassium Ferricyanide, $K_3Fe'''Cy_6$, often called *red prussiate of potash*, is prepared by slowly passing chlorine, with agitation, into a somewhat dilute and cold solution of potassium ferrocyanide, until the liquid acquires a deep reddish-green color, and ceases to precipitate a ferric salt. The solution is evaporated until a skin begins to form upon the surface, then filtered, and left to cool; and the salt is purified by re-crystallization. It forms regular, prismatic, or sometimes tabular crystals, of a beautiful ruby-red tint, permanent in the air, and soluble in 4 parts of cold water: the solution has a dark-greenish color. The crystals burn when introduced into the flame of a candle, and emit sparks. The salt is decomposed by excess of chlorine, and by deoxidizing agents, as sulphuretted hydrogen.

Hydrogen ferricyanide is obtained in the form of a reddish-brown acid liquid, by decomposing lead ferricyanide with sulphurie acid: it is very unstable, and is resolved, by boiling, into hydrated ferric cyanide, an insoluble dark-green powder containing Fe_2Cy_6 . 3 Aq., and hydrocyanic acid. The ferricyanides of *sodium*, *ammonium*, and of the *alkaline earths*, are soluble; those of most of the other metals are insoluble. Potassium ferricyanide, added to a ferric salt, occasions no precipitate, but merely a darkening of the reddish-brown color of the solution; with *ferrous salts*, on the other hand, it gives a deep blue precipitate, consisting of *ferrous ferricyanide*, $Fe_5Cy_{12} . x$ Aq., or $Fe''_3Fe'''_2Cy_{12} . x$ Aq., which, when dry, has a brighter tint than Prussian blue: it is known under the name of *Turnbull's blue*. Hence, potassium ferricyanide is as delicate a test for ferrous salts as the yellow ferrocyanide is for ferric salts.

Cobalticyanides.—This name is applied to a series of compounds analogous to the preceding, containing cobalt in place of iron; a hydrogen-acid has been obtained, and a number of salts, which much resemble the ferricyanides. Several other metals of the same isomorphous family are found capable of replacing iron in these compounds.

Nitroprussides.—The action of nitric acid upon ferrocyanides and ferricyanides gives rise to the formation of a very interesting series of new salts, which were discovered by Dr. Playfair. The general formula of these salts appears to be $M_2(NO)Fe''Cy_5$, which exhibits a close relation with those of the ferro- and ferricyanides.

The formation of the nitroprussides appears to consist in the reduction of the nitric acid to the state of nitrogen dioxide or nitrosyl, NO, which replaces 1 molecule of metallic cyanide, MCy, in a molecule of ferricyanide, $M_3Fe'''Cy_6$. The formation of these salts is attended by the production of a variety of secondary products, such as cyanogen, oxamide, hydrocyanic acid, nitrogen, carbonic acid, &c. One of the finest compounds of this series is the nitroprusside of sodium, $Na_2(NO)Fe''Cy_5$. 2 Aq., which is readily obtained by treating 2 parts of the powdered ferrocyanide with 5 parts of common nitric acid previously diluted with its own volume of water. The solution, after the evolution of gas has ceased, is digested on the water-bath, until ferrous salts no longer yield a blue, but a slate-colored precipitate. The liquid is now allowed to cool, when much potassium nitrate, and occasionally oxamide, is deposited: it is filtered and neutralized with sodium carbonate, which yields a green or brown precipitate, and a ruby-colored filtrate. This, on evaporation, gives a crystallization of the nitrates of potassium and sodium, together with the nitroprusside. The crystals of the

latter are selected and purified by crystallization; they are rhombic and of a splendid ruby color. The soluble nitroprussides strike a most beautiful violet tint with soluble sulphides. This reaction is recommended by Playfair as the most delicate test for alkaline sulphides.

ALCOHOLIC CYANIDES OR HYDROCYANIC ETHERS.

These compounds play an important part in organic chemistry: we have already had occasion to notice them several times in speaking of the conversion of alcohols into acids containing a greater number of carbon-atoms.

The cyanides of univalent alcohol-radicals may also be regarded as compounds of nitrogen with trivalent radicals: hence they are often called *nitriles;* thus:

Hydrogen cyanide	H . CN	=	$(CH)'''N$	Methenyl nitrile.
Methyl cyanide	CH_3 . CN	=	$(C_2H_3)'''N$	Ethenyl nitrile.
Ethyl cyanide	C_2H_5 . CN	=	$(C_3H_5)'''N$	Propenyl nitrile.
Propyl cyanide	C_3H_7 . CN	=	$(C_4H_7)'''N$	Quartenyl nitrile.
Phenyl cyanide	C_6H_5 . CN	=	$(C_7H_5)'''N$	Benzonitrile.

These alcoholic cyanides are produced:

1. By distilling a mixture of potassium cyanide and the potassium-salt of ethylsulphuric or a similar acid:

CNK	+	$SO_4(C_2H_5)K$	=	SO_4K_2	+	$CN . C_2H_5$
Potassium cyanide.		Potassium ethyl-sulphate.		Potassium sulphate.		Ethyl cyanide.

2. By the dehydrating action of phosphoric oxide on the ammonium-salts of the corresponding acids containing the radicals $C_nH_{2n-1}O$ and $C_nH_{2n-7}O$; thus:

$C_2H_3O_2 . NH_4$	—	$2OH_2$	=	C_2H_3N
Ammonium acetate.				Ethenyl nitrile.
$C_7H_5O_2 . NH_4$	—	$2OH_2$	=	C_7H_5N
Ammonium benzoate.				Benzonitrile.

The bodies obtained by these two processes are oily liquids, exhibiting the same properties whether prepared by the first or the second method, excepting that those obtained by the latter have an aromatic fragrant odor, whereas those prepared by the former have a pungent and repulsive odor, due to the presence of certain isomeric compounds, to be noticed farther on. *Methyl cyanide*, *Ethenyl-nitrile*, or *Acetonitrile*, boils at 77° C. (170° F.); *Ethyl cyanide*, or *Propenyl-nitrile*, at 82° C. (180° F.); *Butyl cyanide*, or *Valeronitrile*, at 125°–128° C. (257°–262° F.); *Amyl cyanide*, or *Capronitrile*, at 146° C. (295° F.); *Phenyl cyanide*, or *Benzonitrile*, at 190·6° C. (375° F.).

All these cyanides, when heated with fuming sulphuric acid or sulphuric oxide, undergo the decomposition already mentioned (p. 682), yielding sulpho-acids. By heating with caustic potash or soda, they are resolved into ammonia and the corresponding fatty or aromatic acid, just as hydrocyanic acid similarly treated is resolved into ammonia and formic acid; thus:

CNH	+	$2H_2O$	=	NH_3	+	CH_2O_2
Hydrogen cyanide.						Formic acid.

$CN.C_2H_5$ Ethyl cyanide.	+	$2H_2O$	=	NH_3	+	$C_3H_6O_2$ Propionic acid.
$CN.C_6H_5$ Phenyl cyanide.	+	$2H_2O$	=	NH_3	+	$C_7H_6O_2$ Benzoic acid.

Ethene cyanide, $(C_2H_4)''(CN)_2$, is obtained by distilling potassium cyanide with ethene bromide:

$$C_2H_4Br_2 + 2CNK = 2KBr + C_2H_4(CN)_2.$$

It is a crystalline body, melting at 50°, and converted by alcoholic potash into ammonia and succinic acid:

$$C_2H_4(CN)_2 + 4H_2O = 2NH_3 + C_4H_6O_4.$$

Isocyanides. — On examining the equations just given for the decomposition of the alcoholic cyanides under the influence of alkalies, it is easy to see that the reaction might be supposed to take place in a different way, each cyanide or nitrile yielding, not ammonia and an acid containing the same number of carbon-atoms as itself, but an alcoholic ammonia, or amine, and formic acid; thus:

$CN.C_2H_5$ Ethyl cyanide.	+	$2H_2O$	=	$NH_2C_2H_5$ Ethyl-amine.	+	CH_2O_2 Formic acid.

In the one case the alcohol-radical remains united with the carbon, producing a homologue of formic acid, together with ammonia; in the other it remains united with the nitrogen, producing a homologue of ammonia, together with formic acid.

A class of cyanides exhibiting the second of these reactions has lately been discovered by Dr. Hofmann.* They are obtained by distilling a mixture of an alcoholic ammonia-base and chloroform with alcoholic potash; for example:

C_6H_7N Aniline.	+	$CHCl_3$ Chloro-form.	=	$3HCl$	+	C_7H_5N Phenyl-isocyanide.

The potash serves to neutralize the hydrochloric acid produced, which would otherwise quickly decompose the isocyanide. Phenyl isocyanide, when freed from excess of aniline by oxalic acid, then dried with caustic potash and rectified, is an oily liquid, green by transmitted, blue by reflected light, and having an intolerably pungent and suffocating odor. It is isomeric with benzonitrile, and is resolved by boiling with dilute acids into formic acid and aniline:

$$C_7H_5N + 2H_2O = CH_2O_2 + C_6H_7N.$$

It is a remarkable fact that, whereas the normal alcoholic cyanides are easily decomposed by boiling alkaline solutions, the isocyanides are scarcely altered by alkalies, but are easily hydrated under the influence of acids.

The isocyanides of ethyl and amyl have been obtained by similar processes; also by the action of ethylic and amylic iodides on silver cyanide. They resemble the phenyl compound in their reactions, and are also characterized by extremely powerful odors. The repulsive odor possessed by the normal alcoholic cyanides when prepared by distilling potassium cya-

* Proceedings of the Royal Society, xvi. 144, 148, 150.

nide with the ethyl-sulphate, appears to be due to the presence of small quantities of these isocyanides.

The difference of constitution between the normal cyanides and the isocyanides may be represented by the following formulæ,* taking the methyl compounds for example:

$$C^{iv}\left\{\begin{matrix}N'' \\ CH_3\end{matrix}\right. \qquad\qquad N^{v}\left\{\begin{matrix}C^{iv} \\ CH_3\end{matrix}\right.$$

Cyanide. Isocyanide.

In the isocyanide the carbon belonging to the alcohol-radical is united directly with the nitrogen; in the isocyanide, only through the medium of the carbon belonging to the cyanogen.

This difference of structure may perhaps account for the difference in the reactions of the cyanides and isocyanides under the influence of hydrating agents; thus:

$$C\left\{\begin{matrix}N \\ CH_3\end{matrix}\right. + 2H_2O = NH_3 + C\left\{\begin{matrix}CH_3 \\ O'' \\ OH\end{matrix}\right.$$

Methyl cyanide. Ammonia. Acetic acid.

$$N\left\{\begin{matrix}C \\ CH_3\end{matrix}\right. + 2H_2O = N\left\{\begin{matrix}H_2 \\ CH_3\end{matrix}\right. + C\left\{\begin{matrix}H \\ O \\ OH\end{matrix}\right.$$

Methyl isocyanide. Methylamine. Formic acid.

Cyanic and Cyanuric Acids.

These are two remarkable polymeric bodies, related in a very close and intimate manner, and presenting phenomena of great interest. Cyanic acid is formed as a potassium-salt, in conjunction with potassium cyanide, when cyanogen gas is transmitted over heated hydrate or carbonate of potassium, or passed into a solution of the alkaline base, the reaction resembling that by which potassium chlorate and potassium chloride are generated when chlorine is passed into a solution of potash, (p. 186.) Potassium cyanate is, moreover, formed when the cyanide is exposed to a high temperature with access of air: unlike the chlorate, it bears a full red heat without decomposition.

Cyanic Acid, CNHO, is procured by heating to dull redness in a hard glass retort connected with a receiver cooled by ice, cyanuric acid deprived of its water of crystallization. The cyanuric acid is resolved, without any other product, into cyanic acid, which condenses in the receiver to a limpid, colorless liquid, of exceedingly pungent and penetrating odor, like that of the strongest acetic acid: it even blisters the skin. When mixed with water, it decomposes almost immediately, giving rise to ammonium bicarbonate:

$$CNHO + OH_2 = CO_2 + NH_3.$$

This is the reason why the acid cannot be separated from a cyanate by a stronger acid. A trace of cyanic acid, however, always escapes decomposition, and communicates to the carbon dioxide evolved a pungent smell similar to that of sulphurous acid. The cyanates may be easily distinguished by this smell, and by the simultaneous formation of an ammonia-salt, which remains behind.

Pure cyanic acid cannot be preserved: shortly after its preparation it changes spontaneously, with sudden elevation of temperature, into a solid, white, opaque, amorphous substance, called *cyamelide*. This curious body

* *Naquet*, Laboratory, p. 411.

has the same composition as cyanic acid: it is insoluble in water, alcohol, ether, and dilute acids: it dissolves in strong oil of vitriol by the aid of heat, with evolution of carbon dioxide and production of ammonia; boiled with solution of caustic alkali, it dissolves, ammonia being disengaged, and a mixture of cyanate and cyanurate of the base generated. By dry distillation it is again converted into cyanic acid.

Potassium Cyanate, CNKO. — The best method of preparing this salt is, according to Liebig, to oxidize potassium cyanide with litharge. The cyanide, already containing a portion of cyanate, described at page 704, is re-melted in an earthen crucible, and finely powdered lead oxide added by small portions: the oxide is instantaneously reduced, and the metal, at first in a state of minute division, ultimately collects to a fused globule at the bottom of the crucible. The salt is poured out, and, when cold, powdered and boiled with alcohol; the hot filtered solution deposits crystals of potassium cyanate on cooling. The great deoxidizing power exerted by potassium cyanide at a high temperature promises to render it a valuable agent in many of the finer metallurgic operations.

Another method of preparing the cyanate is to mix dried and finely-powdered potassium ferrocyanide with half its weight of equally dry manganese dioxide; heat this mixture in a shallow iron ladle, with free exposure to air and frequent stirring, until the tinder-like combustion is at an end; and boil the residue in alcohol, which extracts the potassium cyanate.

This salt crystallizes from alcohol in thin, colorless, transparent plates, which suffer no change in dry air, but on exposure to moisture are gradually converted, without much alteration of appearance, into potassium bicarbonate, ammonia being at the same time given off. Water dissolves potassium cyanate in large quantity: the solution is slowly decomposed in the cold, and rapidly at a boiling heat, into potassium bicarbonate and ammonia. When a concentrated solution is mixed with a small quantity of dilute mineral acid, a precipitate falls, consisting of acid potassium cyanurate. Potassium cyanate is reduced to cyanide by ignition with charcoal in a covered crucible. Mixed with solutions of lead and silver, it gives rise to white insoluble cyanates of those metals.

Ammonium cyanate; Urea. — When the vapor of cyanic acid is mixed with excess of ammoniacal gas, a white, crystalline, solid substance is produced, which has all the characters of a true, although not neutral ammonium cyanate. It dissolves in water, and if mixed with an acid, evolves carbon dioxide: with an alkali, it yields ammonia. If the solution be heated, or if the crystals be merely exposed for a certain time to the air, a portion of ammonia is dissipated, and the properties of the compound are completely changed. It may now be mixed with acids without the least sign of decomposition, and does not evolve the smallest trace of ammonia when treated with cold caustic alkali. The result of this curious metamorphosis of the cyanate is *urea*, a product of the animal body, the chief and characteristic constituent of urine. This transformation, the discovery of which is due to Wöhler, is especially interesting as the first instance of the artificial formation of a product of the living organism. The properties of urea, and the most advantageous methods of preparing it, will be found described a few pages hence.

Cyanuric Acid, $C_3N_3H_3O_3$. — The substance called *melam*, of which further mention will be made, is dissolved by gentle heat in concentrated sulphuric acid, the solution mixed with 20 or 30 parts of water, and the whole maintained at a temperature approaching the boiling point, until a specimen of the liquid, on being tried by ammonia, no longer gives a white precipitate: several days are required to effect this change. The liquid, con-

centrated by evaporation, deposits on cooling cyanuric acid, which is purified by re-crystallization. Another, and perhaps simpler method, is to heat dry and pure urea in a flask or retort: the substance melts, boils, gives off ammonia in large quantity, and at length becomes converted into a dirty-white, solid, amorphous mass, which is impure cyanuric acid. This is dissolved by the aid of heat in strong oil of vitriol, and nitric acid added by small portions till the liquid becomes nearly colorless: it is then mixed with water, and left to cool, whereupon the cyanuric acid separates. The urea may likewise be decomposed very conveniently by gently heating it in a tube, while dry chlorine or hydrochloric acid gas passes over it. A mixture of cyanuric acid and sal-ammoniac results, which is separated by dissolving the latter in water.

Cyanuric acid forms colorless efflorescent crystals, seldom of large size, derived from an oblique rhombic prism. It is very little soluble in cold water, and requires 24 parts for solution at a boiling heat: it reddens litmus feebly, has no odor, and but little taste. The acid is tribasic: the crystals contain $C_3N_3H_3O_3 . 2$ Aq., and are easily deprived of their water of crystallization. In point of stability, cyanuric acid offers a most remarkable contrast to its isomer, cyanic acid; it dissolves, as above indicated, in hot oil of vitriol, and even in strong nitric acid, without decomposition, and, in fact, crystallizes from the latter in the anhydrous state. Long-continued boiling with these powerful agents resolves it into ammonia and carbonic acid.

The connection between cyanic acid, urea, and cyanuric acid, may be thus recapitulated:

Ammonium cyanate is converted by heat into urea.

Urea is decomposed by the same means into cyanuric acid and ammonia.

Cyanuric acid is changed by a very high temperature into cyanic acid, one molecule of cyanuric acid splitting into 3 molecules of cyanic acic.

Ethyl Cyanate and Cyanurate. — When a dry mixture of potassium cyanate and ethylsulphate is distilled, a product is obtained which consists of a mixture of the above ethers. They are separated without difficulty, the cyanate boiling at 60° C. (140° F.), while the boiling point of the cyanurate is much higher — namely, 276° C. (528° F.). Ethyl cyanate, $CNO . C_2H_5$, is a mobile liquid, the vapor of which excites a flow of tears. Its formation is represented by the equation,

$$CNOK + SO_4(C_2H_5)K = SO_4K_2 + CNO . C_2H_5.$$

Ethyl cyanurate contains $C_3N_3O_3 . (C_2H_5)_3$: it arises in this reaction from the coalescence of 3 molecules of ethyl cyanate. It may be likewise obtained by distilling a mixture of potassium ethylsulphate and cyanurate. Ethyl cyanurate is a crystalline mass, slightly soluble in water, readily soluble in alcohol and ether, melting at 85° C. (185° F.). By substituting for potassium ethylsulphate, salts of methyl- and amyl-sulphuric acid, the corresponding methyl- and amyl-compounds may be obtained.

The study of the cyanic and cyanuric ethers, which were discovered by Wurtz, has led to very important results, which will be fully described in the section on the Organic Bases.

Fulminic Acid. — This remarkable compound, which is polymeric both with cyanic and cyanuric acids, originates in the peculiar action exercised by nitrous acid upon alcohol in presence of a salt of silver or mercury. The acid itself, or hydrogen fulminate, has not been obtained.

Silver fulminate is prepared by dissolving 40 or 50 grains of silver, which

need not be pure, in about ¾ oz. by measure of nitric acid of sp. gr. 1·37, by the aid of a little heat. To the highly acid solution, while still hot, 2 measured ounces of alcohol are added, and heat is applied until reaction commences. The nitric acid oxidizes part of the alcohol to aldehyde and oxalic acid, becoming itself reduced to nitrous acid, which, in turn, acts upon the alcohol in such a manner as to form nitrous ether, fulminic acid, and water, 1 molecule of nitrous ether and 1 molecule of nitrous acid containing the elements of 1 molecule of fulminic acid and 2 molecules of water:

$$\underset{\text{Ethyl nitrite.}}{NO_2C_2H_5} + \underset{\text{Nitrous acid.}}{NO_2H} = \underset{\text{Fulminic acid.}}{C_2N_2H_2O_2} + 2OH_2.$$

The silver fulminate slowly separates from the hot liquid in the form of small, brilliant, white, crystalline plates, which may be washed with a little cold water, distributed upon separate pieces of filter-paper in portions not exceeding a grain or two each, and left to dry in a warm place. When dry, the papers are folded up and preserved in a box. The only perfectly safe method of keeping the salt is by immersing it in water. Silver fulminate is soluble in 36 parts of boiling water, but the greater part crystallizes out on cooling: it is one of the most dangerous substances known, exploding with fearful violence when strongly heated, or when rubbed or struck with a hard body, or when touched with concentrated sulphuric acid: the metal is reduced, and a large volume of gaseous matter suddenly liberated. Strange to say, it may, when very cautiously mixed with copper oxide, be burned in a tube with as much facility as any other organic substance. Its composition thus determined is expressed by the formula $C_2N_2O_2Ag_2$.

Fulminic acid is bibasic: when silver fulminate is digested with caustic potash, one-half of the silver is precipitated as oxide, and a *silver potassium fulminate*, $C_2N_2O_2AgK$, is produced, which resembles the neutral silver-salt, and detonates by a blow. Corresponding compounds containing sodium or ammonium exist; but a pure fulminate of an alkali-metal has never been formed. If silver fulminate be digested with water and copper, or zinc, the silver is entirely displaced, and a fulminate of the other metal produced. The zinc-salt mixed with baryta-water gives rise to a precipitate of zinc oxide, while *zinco-baric fulminate*, $(C_2N_2O_2)_2Zn''Ba''$, remains in solution. *Mercuric fulminate*, $C_2N_2O_2Hg''$, is prepared by a process very similar to that by which the silver-salt is obtained: one part of mercury is dissolved in 12 parts of nitric acid, and the solution mixed with an equal quantity of alcohol; gentle heat is applied, and if the reaction becomes too violent, it may be moderated by the addition from time to time of more spirit: much carbonic acid, nitrogen, and red vapors are disengaged, together with a large quantity of nitrous ether and aldehyde: these are sometimes condensed and collected for sale, but are said to contain hydrocyanic acid. The mercuric fulminate separates from hot liquid, and after cooling may be purified from an admixture of reduced metal by solution in boiling water and re-crystallization. It much resembles the silver salt in appearance, properties, and degree of solubility. It explodes violently by friction or percussion, but, unlike the silver compound, merely burns with a sudden and almost noiseless flash when kindled in the open air. It is manufactured on a large scale for the purpose of charging *percussion-caps*; sulphur and potassium chlorate, or more frequently nitre, are added, and the powder, pressed into the cap, is secured by a drop of varnish.

The relation of composition between the three isomeric acids are beautifully seen by comparing their silver salts: the first acid is monobasic, the second bibasic, and the third tribasic:

Silver cyanate	$CNOAg$.
Silver fulminate	$C_2N_2O_2Ag_2$.
Silver cyanurate	$C_3N_3O_3Ag_3$.

Until lately, beyond that of identity of composition, no relation was known to exist between fulminic acid and its isomers. Dr. Gladstone has, however, shown that, when a solution of copper fulminate is mixed with excess of ammonia, filtered, treated with sulphuretted hydrogen in excess, and again filtered from the insoluble copper sulphide, the liquid obtained is a mixed solution of urea and ammonium sulphocyanate.

Another view regarding the constitution of fulminic acid was proposed by Gerhardt. The fulminates may be considered as methyl cyanide (aceto-nitrile), in which one atom of hydrogen is replaced by NO_2 and 2 atoms of hydrogen by mercury or silver:

$CNCHHH$	Methyl cyanide.
$CNC(NO_2)Ag_2$ . . .	Silver fulminate.
$CNC(NO_2)Hg''$ . . .	Mercuric fulminate.

This view has received some support by the interesting observation, lately made by Kekulé, that the action of chlorine upon mercuric fulminate gives rise to the formation of chloropicrin, CCl_3NO_2 (p. 533), a substance originally obtained by Stenhouse, which may be viewed as chloroform, the hydrogen of which is replaced by NO_2. The connection of fulminic acid with the methyl series is thus established.

Fulminuric Acid, $C_3N_3H_3O_3$.—This acid, isomeric with cyanuric acid, was discovered simultaneously by Liebig and by Schischkoff. It is obtained by the action of a soluble chloride upon mercuric fulminate. On boiling mercuric fulminate with an aqueous solution of potassium chloride, the mercury-salt gradually dissolves, and the clear solution, after some time, becomes turbid, in consequence of a separation of mercuric oxide; it then contains potassium fulminurate:

$$\underset{\text{Mercuric fulminate.}}{3C_2N_2O_2Hg''} + 8KCl + OH_2 = 4KCl + 2HgCl_2 + Hg''O + \underset{\text{Potassium fulminurate.}}{2C_3N_3O_3HK_2}$$

If, instead of potassium chloride, sodium or ammonium chloride be employed, the corresponding sodium and ammonium-compounds are obtained. The fulminurates crystallize with great facility; they are not explosive.

Fulminuric acid has the same composition as cyanuric acid, but it is monobasic, whereas cyanuric acid is tribasic.

Cyanogen Chlorides.—Chlorine forms with cyanogen, or its elements, two compounds, which are polymeric, and correspond to cyanic and cyanuric acids. *Gaseous cyanogen chloride*, $CyCl$, is formed by passing chlorine gas into anhydrous hydrocyanic acid, or by passing chlorine over moist mercuric cyanide contained in a tube sheltered from the light. It is a permanent and colorless gas at the temperature of the air, of insupportable pungency, and soluble to a very considerable extent in water, alcohol, and ether. At —18° C. (0° F.) it congeals to a mass of colorless crystals, which at —15° C. (5° F.) melt to a liquid whose boiling point is —11·6° C. (13° F.). At the temperature of the air it is condensed to the liquid form under a pressure of four atmospheres, and when long preserved in this condition in hermetically sealed tubes gradually passes into the solid modification.

On passing gaseous cyanogen chloride into a solution of ammonia in anhydrous ether, ammonium chloride is deposited, and the ether contains *cyanamide*, CN_2H_2, in solution, from which it separates on evaporation in the crystalline form. Cyanamide is easily soluble in water, alcohol, and ether; it melts at 40° C. (104° F.).

Solid cyanogen chloride, $C_3N_3Cl_3$, or Cy_3Cl_3, is generated when anhydrous hydrocyanic acid is put into a vessel of chlorine gas, and the whole exposed to the sun: hydrochloric acid is formed at the same time. It forms long colorless needles, which exhale a powerful and offensive odor, compared by some to that of the excrement of mice; it melts at 140° C. (284° F.), and sublimes unchanged at a higher temperature. When heated in contact with water, it is decomposed into cyanuric and hydrochloric acids. It dissolves in alcohol and ether without decomposition.

Cyanogen Bromide and Iodide correspond to the first of the preceding compounds, and are prepared by distilling bromine or iodine with mercuric cyanide. They are colorless, volatile, solid substances, of powerful odor.

Cyanogen Sulphide, C_2N_2S, or Cy_2S, recently obtained by Linnemann by the action of cyanogen iodide upon silver sulphocyanate, crystallizes in transparent, volatile, rhombic plates, having an odor similar to that of cyanogen iodide. It melts at 60°, but decomposes rapidly at a higher temperature; dissolves in ether, alcohol, and water, and separates from hot concentrated solutions, on cooling, in the crystalline form.

Sulphocyanic Acid, CNHS. — This acid is the sulphur analogue of cyanic acid, and, like the latter, is monobasic, the sulphocyanates of monad metals being represented by the formula CNSM.

Potassium sulphocyanate, CNSK. — To prepare this salt, yellow potassium ferrocyanide, deprived of its water of crystallization, is intimately mixed with half its weight of sulphur, and the whole heated to tranquil fusion in an iron pot, and kept for some time in that condition. When cold, the melted mass is boiled with water, which dissolves out a mixture of potassium sulphocyanate and iron sulphocyanate, leaving little behind but the excess of sulphur. This solution, which becomes red on exposure to the air, from oxidation of the iron, is mixed with potassium carbonate, by which the iron is precipitated, and potassium substituted: an excess of the carbonate must be, as far as possible, avoided. The filtered liquid is concentrated, by evaporation over an open fire, to a small bulk, and left to cool and crystallize. The crystals are drained, purified by re-solution, if necessary, or dried by enclosing them, spread on filter-paper, over a surface of oil of vitriol covered with a bell-jar.

The reaction between the sulphur and the potassium ferrocyanide is represented by the equation:

$$K_4Fe''C_6N_6 \quad + \quad S_6 \quad = \quad 4CNSK \quad + \quad (CNS)_2Fe''$$

Another, and even better process, consists in gradually heating to low redness in a covered vessel a mixture of 46 parts of dried potassium ferrocyanide, 32 of sulphur, and 17 of pure potassium carbonate. The mass is exhausted with water, the aqueous solution is evaporated to dryness, and the residue is exhausted with alcohol. The alcoholic liquid deposits splendid crystals on cooling or evaporation.

Potassium sulphocyanate crystallizes in long, slender, colorless prisms, or plates, which are anhydrous: it has a bitter saline taste, and is destitute of poisonous properties: it is very soluble in water and alcohol, and deliquesces when exposed to a moist atmosphere. When heated, it melts to a colorless liquid, at a temperature far below that of ignition.

When chlorine is passed into a strong solution of potassium sulphocyanate, a large quantity of a bulky, deep yellow, insoluble substance, resembling some varieties of lead chromate, is produced, together with potassium chloride; the liquid sometimes assumes a deep-red tint, and emits a pungent vapor, probably cyanogen chloride. The yellow matter may be collected on a filter, well washed with boiling water, and dried: it retains

its brilliancy of tint. It was formerly called *sulphocyanogen*, from its supposed identity with the radical of the sulphocyanates; it is, however, invariably found to contain hydrogen, and is represented by the formula $C_3N_3HS_3$. The yellow substance, now generally called *persulphocyanogen*, is quite insoluble in water, alcohol, and ether: it dissolves in concentrated sulphuric acid, from which it is precipitated by dilution. Caustic potash also dissolves it, with decomposition; acids throw down from this solution a pale-yellow, insoluble body, having acid properties. When heated in the dry state, it evolves sulphur and carbon bisulphide, and leaves a pale, straw-yellow substance, called *hydromellone*, $C_6N_9H_3$, the decomposition being represented by the equation:

$$3C_3N_3HS_3 = 3CS_2 + S_3 + C_6N_9H_3.$$

Hydrogen Sulphocyanate, or *Hydrosulphocyanic Acid*, CNSH, is obtained by decomposing lead sulphocyanate, suspended in water, with sulphuretted hydrogen. The filtered solution is colorless, very acid, and not poisonous; it is easily decomposed, in a very complex manner, by ebullition, and by exposure to the air. By neutralizing the liquid with ammonia, and evaporating very gently to dryness, *ammonium sulphocyanate*, $CNSNH_4$, is obtained as a deliquescent, saline mass. The salt may be conveniently prepared by digesting hydrocyanic acid with yellow ammonium sulphide (containing excess of sulphur), and boiling off the excess of the latter: $2CNH + (NH_4)_2S + S_2 = H_2S + 2CNS(NH_4)$. The sulphocyanates of *sodium*, *barium*, *strontium*, *calcium*, *manganese*, and *iron*, are colorless and very soluble: those of *lead* and *silver* are white and insoluble. A soluble sulphocyanate mixed with a ferric salt gives no precipitate, but causes the liquid to assume a deep blood-red tint: hence the use of potassium sulphocyanate as a test for iron in the state of ferric salt. The red color produced by sulphocyanates in ferric solutions is exactly like that caused under similar circumstances by meconic acid. The two substances may, however, be readily distinguished by the addition of a solution of gold chloride, which destroys the color produced by sulphocyanates. The ferric meconate may also be distinguished from the sulphocyanide, as Everitt has shown, by an addition of corrosive sublimate, which bleaches the sulphocyanate, but has little effect upon the meconate. This is a point of considerable practical importance, as in medico-legal inquiries, in which evidence of the presence of opium is sought for in complex organic mixtures, the detection of meconic acid is usually the object of the chemist: and since traces of alkaline sulphocyanide are to be found in the saliva, it becomes very desirable to remove that source of error and ambiguity.

The great facility with which hydrocyanic acid may be converted into ammonium sulphocyanate enables us to ascertain its presence by the iron test just described. The cyanide to be examined is mixed in a watch-glass with some hydrochloric acid, and covered with another watch-glass, to which a few drops of yellow ammonium sulphide adhere. On heating the mixture, hydrocyanic acid is disengaged, which combines with the ammonium sulphide, and produces ammonium sulphocyanate: this, after expulsion of the excess of sulphide, yields the red color with solution of ferric chloride.

Sulphocyanic Ethers. — These ethers exhibit isomeric modifications, probably analogous to those of the alcoholic cyanides and isocyanides (p. 711). The normal sulphocyanates of methyl and its homologues were discovered by Cahours;* and quite recently Hofmann has obtained the corresponding isosulphocyanates.† The same chemist some years ago obtained

* Ann. Chim. Phys. [3], viii. 264.
† Proceedings of the Royal Society, xvi. 254.

phenyl isosulphocyanate.* Allyl isosulphocyanate has long been known as a natural product.

Normal Ethyl Sulphocyanate, $C\left\{\begin{matrix}N\\SC_2H_5\end{matrix}\right.$, is obtained by saturating a concentrated solution of potassium sulphocyanate with ethyl chloride:

$$C\left\{\begin{matrix}N\\SK\end{matrix}\right. + C_2H_5Cl = KCl + C\left\{\begin{matrix}N\\SC_2H_5\end{matrix}\right.;$$

also by distilling a mixture of calcium ethylsulphate and potassium sulphocyanate. It is a mobile, colorless, strongly refracting liquid, having a somewhat pungent odor, like that of mercaptan. It boils at 146° C. (295° F.) With ammonia it does not combine directly, but yields products of decomposition.

The methyl and amyl sulphocyanic ethers resemble the ethyl compound, and are obtained by similar processes. The methyl ether boils at about 132° C. (270° F.); the amyl ether at 197° C. (387° F.).

Ethyl Isosulphocyanate, $N\left\{\begin{matrix}(CS)''\\C_2H_5\end{matrix}\right.$, is produced by distilling diethyl-sulphocarbamide with phosphoric oxide, which abstracts ethylamine:

$$N_2\left\{\begin{matrix}(CS)''\\(C_2H_5)_2\\H_2\end{matrix}\right. - N\left\{\begin{matrix}C_2H_5\\H_2\end{matrix}\right. = N\left\{\begin{matrix}(CS)''\\C_2H_5\end{matrix}\right.$$

Diethyl-sulphocarbamide. Ethylamine. Ethyl isosulphocyanate.

This ether differs essentially in all its properties from ethyl sulphocyanate. It boils at 134° C. (273° F.), and has a powerfully irritating odor, like that of mustard-oil, and quite different from that of normal ethyl-sulphocyanate. It unites directly with ammonia in alcoholic solution, forming ethylsulphocarbamide, $N_2(CS)''(C_2H_5)H_3$, and forms similar compounds with methylamine and ethylamine. The pungent odor and the direct combination with ammonia and amines, are characteristic of all the ethers of this group.

Phenyl Isosulphocyanate, $N(CS)''(C_6H_5)$, is obtained by distilling phenylsulphocarbamide, $N_2(CS)''(C_6H_5)H_3$, with phosphoric oxide: naphthyl isosulphocyanate, $N(CS)''(C_{10}H_7)$, in like manner from dinaphthylsulphocarbamide. The former boils at 220° C. (428° F.).

Allyl Isosulphocyanate, $N\left\{\begin{matrix}(CS)''\\C_3H_5\end{matrix}\right.$. — This is the intensely pungent volatile oil obtained by distilling the seeds of black mustard with water. It does not exist ready formed in the seeds, but is produced by the decomposition of myronic acid under the influence of myrosin, an albuminous substance analogous to the synaptase of bitter almonds (see p. 579). The same compound, or perhaps its isomer, normal ethylsulphocyanate, is produced by the action of potassium sulphocyanate or silver sulphocyanate, on allyl iodide or allyl oxide. Oil of mustard is a transparent, colorless, strongly refracting oil, possessing in the highest degree the sharp penetrating odor of black mustard. The smallest quantity of the vapor excites tears, and is apt to produce inflammation of the eyes. It has a burning taste, and rapidly blisters the skin. Its specific gravity is 1·009 at 15°. It boils at 148° C. (298° F.). It is sparingly soluble in water, easily soluble in alcohol and ether; dissolves sulphur and phosphorus when heated, and deposits them in the crystalline state, on cooling. It is violently oxidized by nitric and by nitromuriatic acids. Heated in a sealed tube with potassium monosulphide, it yields potassium sulphocyanate and *allyl sulphide* (volatile oil of garlic, p. 545):

$$2NCS(C_3H_5) + K_2S = 2CNSK + (C_3H_5)_2S.$$

* Proceedings of the Royal Society, ix. 274, 487.

It likewise yields garlic oil when decomposed by potassium. Heated to 120° in a sealed tube with pulverized soda-lime, it yields sodium sulphocyanate and *allyl oxide*, the oxidized constituent of garlic oil:

$$2NCS(C_3H_5) + Na_2O = 2CNSNa + (C_3H_5)_2O.$$

Aqueous potash, soda, baryta, and the oxides of lead, silver, and mercury, in presence of water, convert oil of mustard into *sinapoline*, $C_7H_{12}N_2O$, with formation of metallic sulphide and carbonate; thus:

$$2NCS(C_3H_5) + 3PbO + OH_2 = 2PbS + CO_3Pb + C_7H_{12}N_2O.$$

Sinapoline is a basic substance, which crystallizes in colorless plates, soluble in water and alcohol, and having a distinct alkaline reaction.

Oil of mustard unites readily with ammonia, forming *thiosinamine*, $C_4H_5NS.NH_3$, or *allyl-sulphocarbamide*, $N_2\left\{\begin{matrix}(CS)\\C_3H_5,\\H_3\end{matrix}\right.$ which is also a basic compound, forming colorless prismatic crystals, having a bitter taste and soluble in water. The solution does not affect test-paper. Thiosinamine melts when heated, but cannot be sublimed. Acids combine with it, but do not form crystallizable salts: the double salts of the hydrochloride with platinic and mercuric chloride are the most definite.

Thiosinamine is decomposed by metallic oxides, as lead oxide or mercuric oxide, with production of a metallic sulphide and *sinamine*, $C_4H_6N_2$, a basic compound which crystallizes very slowly from a concentrated aqueous solution in brilliant, colorless crystals containing water. It has a powerfully bitter taste, is strongly alkaline to test-paper, and decomposes ammonium salts at the boiling heat. Its oxalate is crystallizable. The formation of sinamine from thiosinamine by the action of mercuric oxide is represented by the equation $C_4H_8N_2S + HgO = HgS + OH_2 + C_4H_6N_2$.

Seleniocyanates. — A series of salts containing selenium, and corresponding in composition and properties with the sulphocyanates, have been discovered and examined by Mr. Crookes.*

Melam. — This name is given by Liebig to a buff-colored, insoluble, amorphous substance, obtained by the distillation of ammonium sulphocyanate at a high temperature. It may be prepared in large quantity by intimately mixing 1 part of perfectly dry potassium sulphocyanate with 2 parts of powdered sal-ammoniac, and heating the mixture for some time in a retort or flask: carbon bisulphide, ammonium sulphide, and sulphuretted hydrogen, are disengaged and volatilized, while a mixture of melam, potassium chloride, and sal-ammoniac remains: the two latter substances are removed by washing with hot water. Melam contains $C_6H_9N_{11}$: it dissolves in concentrated sulphuric acid, and gives, by dilution with water and long boiling, cyanuric acid. The same substance is produced, with disengagement of ammonia, when melam is fused with potassium hydrate. When strongly heated, melam is resolved into mellone and ammonia.

If melam be boiled for a long time in a moderately strong solution of caustic potash, until the whole has dissolved, and the liquid be then concentrated, a crystalline substance separates on cooling, which is called *melamine*. By re-crystallization it is obtained in colorless crystals, having the figure of an octohedron with rhombic base: it is but slightly soluble in cold water, fusible by heat. Melamine is also formed on heating cyanamide to 150° C. (302° F.), and even on evaporating an aqueous solution of that substance. It contains $C_3H_6N_6$, and acts as a base, combining with acids to form crystallizable compounds. A second basic substance, called

* Journal of the Chemical Society, iv. 12,

ammeline, very similar in properties to melamine, is found in the alkaline mother-liquor from which the melamine has separated: it is thrown down on neutralizing the liquid with acetic acid. The precipitate, dissolved in dilute nitric acid, yields crystals of ammeline nitrate, from which the pure ammeline may be separated by ammonia. It forms a brilliant white powder composed of minute needles, insoluble in water and alcohol, and contains $C_3H_5N_5O$. When ammeline is dissolved in concentrated sulphuric acid, and the solution mixed with a large quantity of water, or, better, spirit of wine, a white, insoluble powder falls, which is called *ammelide*, and is found to contain $C_6H_9N_9O_3$.

By the action of acids or alkalies, melamine may be converted into ammeline, ammelide, and, lastly, into cyanuric acid, water being assimilated and ammonia evolved:

$$\underset{\text{Melamine.}}{C_3H_6N_6} + H_2O = \underset{\text{Ammeline.}}{C_3H_5N_5O} + NH_3$$

$$\underset{\text{Ammeline.}}{2C_3H_5N_5O} + H_2O = \underset{\text{Ammelide.}}{C_6H_9N_9O_3} + NH_3$$

$$\underset{\text{Ammelide.}}{C_6H_9N_9O_3} + 3H_2O = \underset{\text{Cyanuric acid.}}{2C_3H_3N_3O_3} + 3NH_3.$$

Mellone and its Compounds. — The formation of mellone as a residuary product of the action of heat on persulphocyanogen, and upon melam, has been already mentioned. This substance, which does not appear to have been obtained in a state of purity, possesses the properties of an organic radical. At a high temperature it combines directly with potassium, producing a well-defined saline compound, *tripotassic mellonide*, $C_9H_{13}K_3$, and the same salt is produced in the action of mellone upon potassium bromide and iodide, bromine and iodine being liberated. A better method of preparing it consists in fusing crude mellone with potassium sulphocyanate. It may also be produced by fusing the ferrocyanide with half its weight of sulphur. The fused mass obtained by either process is dissolved in boiling water, from which the tri-potassic mellonide crystallizes on cooling, and may be purified by repeated crystallization. Acetic acid converts this salt into dipotassic mellonide, $C_9H_{13}K_2H$, which is also soluble. Hydrochloric acid produces the monopotassic salt, $C_9N_{13}KH_2$, which is insoluble. These three salts stand to each other in the same relation as the several salts of phosphoric and cyanuric acids. Tripotassic mellonide produces with soluble silver-salts a white precipitate, $C_9N_{13}Ag_3$; with lead-salts and mercury-salts, precipitates containing respectively $C_{18}N_{26}Pb_3$, and $C_{18}N_{26}Hg_3$. The latter dissolved in hydrocyanic acid, and treated with sulphuretted hydrogen, yields hydromellonic acid, $C_9N_{13}H_3$. It is known only in solution, which has an acid taste: on evaporation it is decomposed.

UREA. — URIC ACID AND ITS PRODUCTS.

These bodies are closely connected with the cyanogen-compounds, and may be most conveniently discussed in the present place.

Urea, CN_2H_4O. — Urea may be extracted from its natural source, the urine, or it may be prepared by artificial means. Fresh urine is concentrated in a water-bath, until reduced to an eighth or a tenth of its original volume, and filtered through cloth from the insoluble deposits of urates and phosphates. The liquid is mixed with about an equal quantity of a strong solution of oxalic acid in hot water, and the whole vigorously agi-

tated and left to cool. A very copious fawn-colored crystalline precipitate of *urea oxalate* is obtained, which may be placed upon a cloth filter, slightly washed with cold water, and pressed. This is to be dissolved in boiling water, and powdered chalk added until effervescence ceases, and the liquid becomes neutral. The solution of urea is filtered from the insoluble calcium oxalate, warmed with a little animal charcoal, again filtered, and concentrated by evaporation, avoiding ebullition, until crystals form on cooling: these are purified by a repetition of the last part of the process. Urea may be extracted in great abundance from the urine of horses and cattle duly concentrated, and from which the hippuric acid has been separated by addition of hydrochloric acid; oxalic acid then throws down the oxalate in such quantity as to render the whole semi-solid. Another process consists in precipitating the evaporated urine with concentrated nitric acid, when *urea nitrate* is precipitated, which is purified by re-crystallization with animal charcoal, and, lastly, decomposed by barium carbonate, whereby a mixture of barium nitrate and urea is formed, which is to be evaporated to dryness on the water-bath, and exhausted with hot alcohol; the urea then crystallizes on cooling.

Urea is produced artificially by heating a solution of ammonium cyanate. The following method of proceeding yields it in any quantity that can be desired. Potassium cyanate, prepared by Liebig's process (p. 713), is dissolved in a small quantity of water, and a quantity of dry neutral ammonium sulphate, equal in weight to the cyanate, is added. The whole is evaporated to dryness in a water-bath, and the dry residue boiled with strong alcohol, which dissolves out the urea, leaving the potassium sulphate and the excess of ammonium sulphate untouched. The filtered solution, concentrated by distilling off a portion of the spirit, deposits the urea in beautiful crystals of considerable size.

Urea forms transparent, colorless, four-sided prisms, which are anhydrous, soluble in an equal weight of cold water, and in a much smaller quantity at a high temperature. It is also readily dissolved by alcohol. It is inodorous, has a cooling saline taste, and is permanent in the air, unless the latter be very damp. When heated it melts, and at a higher temperature decomposes, with evolution of ammonia and ammonium cyanate; cyanuric acid remains, which bears a much greater heat without change. The solution of urea is neutral to test-paper: it is not decomposed in the cold by alkalies or by calcium hydrate, but at a boiling heat emits ammonia, and forms a metallic carbonate. The same change happens by fusion with the alkaline hydrates, and when urea is heated with water, in a sealed tube, to a temperature above 100°:

$$COH_4N_2 + H_2O = CO_2 + 2NH_3.$$

Urea contains, in fact, the elements of ammonium carbonate *minus* the elements of water: $CO_3(NH_4)_2 - 2H_2O$, and has accordingly been supposed to be identical with carbamide. Recent experiments have shown, however, that it is isomeric, not identical with that compound, inasmuch as, when heated with a large excess of potassium permanganate in presence of much free alkali, it gives off all its nitrogen in the free state as gas, whereas when amides and ammonium-salts are thus treated, the whole of the nitrogen is oxidized to nitric acid.* The difference of constitution between the three isomeric compounds — ammonium cyanate, urea, and carbamide — may perhaps be represented by the following formulæ:

$$C\begin{cases} N''' \\ ONH_4 \end{cases} \qquad C\begin{cases} (NH)'' \\ NH_2 \\ OH \end{cases} \qquad C\begin{cases} NH_2 \\ NH_2 \\ O'' \end{cases}$$

Ammonium cyanate. Urea. Carbamide.

* *Wanklyn* and *Gamgee*, Chem. Soc. Journal [2], vi. 25.

A solution of pure urea shows no tendency to change by keeping, and is not decomposed by boiling; in the urine, on the other hand, where it is associated with putrefiable organic matter, as mucus, the case is different. In putrid urine no urea can be found, but enough ammonium carbonate to cause brisk effervescence with an acid; and if urine, in a recent state, be long boiled, it gives off ammonia and carbonic acid from the same source.

Urea is instantly decomposed by *nitrous acid* into carbon dioxide, nitrogen, and water: $COH_4N_2 + 2NO_2H = CO_2 + 2N_2 + 3H_2O$; this decomposition explains the use of urea in preparing nitric ether (p. 526). When *chlorine gas* is passed over melted urea, hydrochloric acid and nitrogen are evolved, and there remains a mixture of sal-ammoniac and cyanuric acid:

$$6COH_4N_2 + 3Cl_2 = 2C_3H_3N_3O_3 + 4NH_4Cl + 2HCl + N_2;$$

but by chlorine in presence of water, or by *hypochlorous acid*, it is resolved into hydrochloric acid, carbon dioxide, water, and nitrogen:

$$COH_4N_2 + 3ClHO = 3HCl + CO_2 + 2H_2O + N_2.$$

Urea acts as a base: with *nitric acid* it forms a sparingly soluble compound, which crystallizes, when pure, in small, indistinct, colorless plates, containing $COH_4N_2 . NO_3H$. When colorless nitric acid is added to urine concentrated to a fourth or a sixth of its volume, and cold, the nitrate crystallizes out in large, brilliant, yellow laminæ, which are very insoluble in the acid liquid. The production of this nitrate is highly characteristic of urea. The *oxalate*, $(COH_4N_2)_2 . C_2H_2O_4$, when pure, crystallizes in large, transparent, colorless plates, which have an acid reaction, and are sparingly soluble. Urea forms several compounds with metallic salts, *e. g.*, with those of mercury. On mixing a liquid containing urea with a solution of *mercuric nitrate*, a white precipitate is formed consisting of $COH_4N_2 . 2HgO$. If the nitric acid which is thus set free be neutralized by the addition of an alkali or baryta-water, the whole of the urea is removed from the liquid in the form of the above compound. Liebig has based upon this reaction a process of determining the amount of urea in urine: 2 volumes of urine are mixed with 1 volume of a baryta-solution prepared with 2 volumes baryta-water saturated in the cold, and 1 volume of a solution of barium-nitrate also saturated in the cold; the liquid is filtered from the precipitated sulphate and phosphate of barium; and a graduated solution of mercuric nitrate is added to a measured quantity of this filtered liquid (about 15 c.c.) till a sample taken out gives a yellow precipitate with sodium carbonate. It is convenient to dilute the mercuric solution to such a degree that 1 cubic centimetre of it shall correspond to 0·01 grm. of urea.*

A series of substances analogous to urea, which are known under the names of methyl-urea, ethyl-urea, biethyl-urea, &c., will be noticed in the section on Organic Bases.

Uric Acid, $C_5N_4H_4O_3$; formerly called *Lithic acid.* — This acid is a product of the animal organism, and has never been formed by artificial means. It may be prepared from human urine by concentration and addition of hydrochloric acid, and crystallizes out after some time in the form of small, reddish, translucent grains, very difficult to purify. A much preferable method is, to employ the solid white excrement of serpents, which can be easily procured: this consists almost entirely of uric acid and ammonium urate. It is reduced to powder, and boiled in dilute solution of caustic potash: the liquid, filtered from the insignificant residue of feculent

* Respecting certain precautions to be observed in performing this process, see the article "Urine," by Dr. Michael Foster, in Watts's Dictionary of Chemistry.

matter and earthy phosphates, is mixed with excess of hydrochloric acid, boiled for a few minutes, and left to cool. The product is collected on a filter, washed until free from potassium chloride, and dried by gentle heat.

Uric acid, thus obtained, forms a glistening, snow-white powder, tasteless, inodorous, and very sparingly soluble. It is seen under the microscope to consist of minute, but regular crystals. It dissolves in concentrated sulphuric acid without apparent decomposition, and is precipitated by dilution with water. By destructive distillation, uric acid yields cyanic acid, hydrocyanic acid, carbon dioxide, ammonium carbonate, and a black coaly residue, rich in nitrogen. By fusion with potassium hydrate, it yields potassium carbonate, cyanate, and cyanide. When treated with nitric acid and with lead dioxide, it undergoes decomposition in a manner to be presently described.

Uric acid is bibasic: its most important salts are those of the alkali-metals. *Acid potassium urate*, $C_5N_4H_3KO_3$, is deposited from a hot saturated solution of uric acid in the dilute alkali, as a white, sparingly soluble, concrete mass, composed of minute needles: it requires about 500 parts of cold water for solution, is rather more soluble at a high temperature, and much more soluble in excess of alkali. *Sodium urate* resembles the potassium-salt: it forms the chief constituent of the gouty concretions in the joints called *chalk-stones*. *Ammonium urate* is also a sparingly soluble compound, requiring for solution about 1000 parts of cold water: the solubility is very much increased by the presence of a small quantity of certain salts, as sodium chloride. The most common of the urinary deposits, forming a buff-colored or pinkish cloud or muddiness, which disappears by re-solution when the urine is warmed, consists of a mixture of different urates.

Uric acid is perfectly well characterized, even when in very small quantity, by its behavior with nitric acid. A small portion mixed with a drop or two of nitric acid in a small porcelain capsule dissolves with copious effervescence. When this solution is cautiously evaporated nearly to dryness, and, after the addition of a little water, mixed with a slight excess of ammonia, a deep-red tint of murexide is immediately produced.

Impure uric acid, in a remarkable state of decomposition, is now imported into this country, in large quantities, for use as a manure, under the name of *guano* or *huano*. It comes chiefly from the barren and uninhabited islets of the western coast of South America, and is the production of the countless birds that dwell undisturbed in those regions. The people of Peru have used it for ages. Guano usually appears as a pale-brown powder, sometimes with whitish specks: it has an extremely offensive odor, the strength of which, however, varies very much. It is soluble in great part in water, and the solution is found to be extremely rich in oxalate of ammonia, the acid having been generated by a process of oxidation. Guano also contains a peculiar substance called *guanine*, which will be described further on.

Products formed from Uric Acid by Oxidation, &c.

Uric acid is remarkable for the facility with which it is altered by oxidizing agents, and the great number of definite and crystallizable compounds obtained in this manner, or by treating the immediate products of oxidation with acids, alkalies, reducing agents, &c. The following is a list of most of the compounds thus produced: —

Uric acid	$C_5N_4H_2O_3 . H_2$*
Pseudo-uric acid	$C_5N_4H_5O_4 . H$
Uroxanic acid	$C_5N_4H_8O_6 . H_2$
Alloxan	$C_4N_2H_2O_4$
Alloxanic acid	$C_4N_2H_2O_5 . H_2$
Alloxantin	$C_8N_4H_4O_7 . 3\,Aq.$
Barbituric acid	$C_4N_2H_2O_3 . H_2$
Bromobarbituric acid	$C_4N_2H_2BrO_3 . H$
Dibromobarbituric acid	$C_4N_2H_2Br_2O_3$
Violuric acid	$C_4N_3H_2O_4 . H$
Dilituric acid	$C_4N_3H_2O_5 . H$
Violantin	$C_9N_6H_6O_9$
Dialuric acid	$C_4N_2H_3O_4 . H$
Uramil	$C_4N_3H_5O_3$

Thionuric acid	$C_4N_3H_3O_6S . H_2$
Hydurilic acid	$C_4N_4H_4O_6 . H_2$
Allantoin	$C_4N_4H_6O_3$
Glycoluril	$C_4N_4H_6O_2$
Mycomelic acid	$C_4N_4H_3O_2 . H$
Oxaluric acid	$C_3N_2H_3O_4 . H$
Allanturic acid	$C_3N_2H_3O_3 . H$
Hydantoin	$C_3N_2H_4O_2$
Hydantoic acid	$C_3N_2H_5O_3 . H$
Alliturie acid	$C_6N_4H_5O_4 . H$
Leucoturic acid	$C_6N_4H_3O_5 . H$
Parabanic acid	$C_3N_2H_2O_3$
Dibarbituric acid	$C_8N_4H_4O_5 . H_2$
Murexide	$C_8N_6H_8O_6$
Mesoxalic acid	$C_3O_5 . H_2$

When uric acid is subjected to the action of an oxidizing agent in presence of water, it gives up two of its hydrogen-atoms to the oxidizing agent, while the dehydrogenized residue (which may be called *dehyduric acid*) reacts with water to form *mesoxalic acid* and *urea:*

$$\underset{\text{Dehyduric acid.}}{C_5N_4H_2O_3} + 4H_2O = \underset{\text{Mesoxalic acid.}}{C_3H_2O_5} + \underset{\text{Urea.}}{2CN_2H_4O}$$

The separation of the urea generally takes place, however, by two stages, the first portion being removed more easily than the second; thus, when dilute nitric acid acts upon uric acid, alloxan is produced; and this, when heated with baryta-water, is further resolved into mesoxalic acid and urea:

$$\underset{\text{Dehyduric acid.}}{C_5N_4H_2O_3} + 2H_2O = \underset{\text{Alloxan.}}{C_4N_2H_2O_4} + \underset{\text{Urea.}}{CN_2H_4O}$$

$$\underset{\text{Alloxan.}}{C_4N_2H_2O_4} + 2H_2O = \underset{\text{Mesoxalic acid.}}{C_3H_2O_5} + \underset{\text{Urea.}}{CN_2H_4O}$$

Moreover, the urea is frequently resolved into carbonic acid and ammonia by the action of the acids or alkalies present. Alloxan is a *monureide* of mesoxalic acid—that is to say, it is a compound of that acid with one molecule of urea minus $2H_2O$; and the hypothetical dehyduric acid is the *diureide* of the same acid, derived from it by addition of 1 molecule of urea and subtraction of 4 molecules of water. Now, by hydrogenizing mesoxalic acid, we obtain *tartronic acid*, $C_3H_4O_5$ (p. 668); and by hydrogenizing alloxan, we obtain *dialuric acid*, which two bodies, accordingly, bear to uric acid the same relation that mesoxalic acid and urea bear to dehyduric acid; thus:

$C_3H_2O_5$ Mesoxalic acid.	$C_4N_2H_2O_4$ Alloxan.	$C_5N_4H_2O_3$ Dehyduric acid.
$C_3H_4O_5$ Tartronic acid.	$C_4N_2H_4O_4$ Dialuric acid.	$C_5N_4H_4O_3$; Uric acid.

and just as the hypothetical dehyduric acid yields mesoxalic acid and alloxan, so should actual uric acid yield tartronic and dialuric acids. These bodies, however, have not been obtained by the direct breaking up of uric

* The basicity of the several acids in this table is indicated by the number of hydrogen-atoms to the right of the point.

acid, but only by rehydrogenizing the mesoxalic acid and alloxan which result from the breaking up of its dehydrogenized product. Provisionally, however, dialuric and uric acids may be regarded as tartron-urcide and tartron-diureide respectively.

The several bodies just mentioned are typical of three well-defined classes of compounds, to one or other of which an immense number of uric acid products may be referred. First, there is the class of simple non-nitrogenous acids, or *an-ureides*, like tartronic and mesoxalic acid; secondly, there is a class of bodies containing a residue of the acid plus one residue of urea—these are the *mon-ureides*, such as dialuric acid and alloxan; and, lastly, the class of bodies containing a residue of the acid plus two residues of urea, or the *di-ureides*, such as uric acid itself.

Mesoxalic acid, the most complex non-nitrogenous product obtainable directly from uric acid, constitutes the third term in the following series:

CH_2O_3	$C_2H_2O_4$	$C_3H_2N_5$,
Carbonic.	Oxalic.	Mesoxalic.

each of which contains 1 atom of carbon monoxide, CO, more than the preceding. Now, when mesoxalic acid is acted upon by nascent oxygen, its excess of carbon monoxide is removed in the form of carbon dioxide, and it is thus converted into oxalic acid:

$$C_3H_2O_5 + O = CO_2 + C_2H_2O_4.$$

Hence, when uric acid is subjected to a more active oxidation than that which suffices to produce mesoxalic acid, we obtain oxalic acid, which may occur either in its simple anureide state, or conjugated with 1 molecule of urea to form a monureide, such as *parabanic acid;* or with 2 molecules of urea to form a diureide, such as *mycomelic acid*, a body related to oxalic acid just as uric acid is related to mesoxalic acid.

In like manner, when uric acid is subjected to a still more powerful oxidation than suffices to produce oxalic acid, we obtain carbonic acid, which, like oxalic and mesoxalic acids, is also capable of giving rise to ureides. No ureide of carbonic acid has, indeed, yet been formed directly from uric acid, the active treatment required to effect the complete oxidation of the uric acid producing also a separation from one another of the resulting carbonic acid and urea, which, however, may be obtained in combination by other means. *Allophanic acid*, for instance, the ethylic ether of which is obtained by passing the vapor of cyanic acid into absolute alcohol, is a monureide of carbonic acid; but no diureide of this acid appears to have been yet produced.

Alloxan, the monureide of mesoxalic acid above mentioned, is formed from mesoxalate of urea by elimination of two molecules of water; but there is another monureide, namely, *alloxanic acid*, which differs from the original salt by only one molecule of water. Similarly, oxalic acid forms two monureides—namely, *parabanic acid* or *paraban*, analogous to alloxan; and *oxaluric acid*, analogous to alloxanic acid. Carbonic acid, however, forms but a single ureide, which is produced by the elimination of only one molecule of water, and accordingly belongs to the same series as the oxaluric and alloxanic acids; thus:

Acids.	*Ureides.*
CH_2O_3, Carbonic.	$C_2N_2H_4O_3$, Allophanic.
$C_2H_2O_4$, Oxalic.	$C_3N_2H_4O_4$, Oxaluric. $C_3N_2H_2O_3$, Paraban.
$C_3H_2O_5$, Mesoxalic.	$C_4N_2H_4O_5$, Alloxanic. $C_4N_2H_2O_4$, Alloxan.

Similarly, among the diurcides, some are formed from the corresponding monureides by elimination of one molecule, and others by elimination of two molecules of water.

Mesoxalic acid, as already observed, is convertible, by deoxidation or hydrogenation, into tartronic acid, and by pushing the deoxidation a stage farther, *malonic acid* (p. 661) is obtained, both of which acids are capable of forming monureides and diureides; and, in a similar manner, oxalic and carbonic acids furnish a variety of similar deoxidation-products.

Of the numerous compounds belonging to the uric acid group thus produced, the most important are included in the following table,* which is divided perpendicularly into three columns of an-ureides, mon-ureides, and di-ureides, and horizontally into three layers of carbonic, oxalic, and mesoxalic products. The compounds connected by dotted lines differ in composition from one another by an excess or deficit of one molecule of urea minus one molecule of water, while those standing on the same level in the adjoining columns, and unconnected by dotted lines, differ from one another by an excess or deficit of one molecule of urea minus two molecules of water.

An-ureides.	*Mon-ureides.*	*Di-ureides.*
CH_2O_3, Carbonic	$C_2N_2H_4O_3$, Allophanic.	
	$C_3N_2H_6O_2$, Aceturea.	
	$C_3N_2H_6O_3$, Glycoluric.	$C_4N_4H_6O_2$, Glycoluril.
		$C_4N_4H_6O_3$, Allantoïn.
$C_2H_4O_2$, Acetic.		
$C_2H_4O_3$, Glycollic.	$C_3N_2H_4O_2$, Hydantoïn.	
$C_2H_4O_4$, Glyoxylic.	$C_3N_2H_4O_3$, Lantanuric.	$C_4N_4H_4O_2$, Mycomelic.
	$C_3N_2H_4O_4$, Oxaluric.	
$C_2H_2O_3$, Glyoxalic.		
$C_2H_2O_4$, Oxalic.	$C_3N_2H_2O_3$, Parabanic.	
		$C_5N_4H_4O$, Hypoxanthine.
$C_3H_4O_4$, Malonic.	$C_4N_2H_4O_3$, Barbituric.	$C_5N_4H_4O_2$, Xanthine.
$C_3H_4O_5$, Tartronic.	$C_4N_2H_4O_4$, Dialuric.	$C_5N_4H_4O_3$, Uric acid.
	$C_4N_2H_4O_5$, Alloxanic.	$C_5N_4H_6O_4$, Pseudo-uric.
$C_3H_2O_5$, Mesoxalic.	$C_4N_2H_2O_4$, Alloxan.	

Between some of the consecutive monureides shown in this table, there exist bodies formed by the union of the two consecutive monureides, with elimination of water. Such is the mode of formation of *allituric*, *lantanuric*, and *hydurilic acids*, and of *alloxantin;* thus:

$C_6N_4H_6O_4$ Allituric acid.	=	$C_3N_2H_4O_2$ Hydantoïn.	+	$C_3N_2H_4O_3$ Lantanuric acid.	—	H_2O
$C_6N_4H_4O_5$ Leucoturic acid.	=	$C_3N_2H_4O_3$ Lantanuric acid.	+	$C_3N_2H_2O_3$ Parabanic acid.	—	H_2O
$C_8N_4H_6O_6$ Hydurilic acid.	=	$C_4N_2H_4O_3$ Barbituric acid.	+	$C_4N_2H_4O_4$ Dialuric acid.	—	H_2O
$C_8N_4H_4O_7$ Alloxantin.	=	$C_4N_2H_4O_4$ Dialuric acid.	+	$C_4N_2H_2O_4$ Alloxan.	—	H_2O

* This table, together with the preceding view of the relations between the several derivatives of uric acid, is taken from Odling's "Lectures on Animal Chemistry." London, 1866, pp. 129–135.

The following is a description of some of the more important compounds above enumerated:

Allantoïn, $C_4N_4H_6O_3$. — This substance, which contains the elements of 2 molecules of ammonium oxalate minus 5 molecules of water [$2C_2(NH_4)_2O_4 - 5H_2O$], is contained in the allantoïc liquid of the fœtal calf and in the urine of the sucking calf. It is produced artificially, together with oxalic acid and urea, by boiling uric acid with lead dioxide and water:

$$\underset{\text{Uric acid.}}{2C_5N_4H_4O_3} + 3O_2 + 5H_2O = \underset{\text{Allantoïn.}}{C_4N_4H_6O_3} + \underset{\text{Oxalic acid.}}{2C_2H_2O_4} + \underset{\text{Urea.}}{2CN_2H_4O_3}$$

The liquid filtered from lead oxalate, and duly concentrated by evaporation, deposits on cooling crystals of allantoïn, which are purified by resolution and the use of animal charcoal. The mother-liquor, when further concentrated, yields crystals of pure urea. Allantoïn forms small but most brilliant prismatic crystals, which are transparent and colorless, destitute of taste, and without action on vegetable colors. It dissolves in 160 parts of cold water, and in a smaller quantity at the boiling heat. It is decomposed by boiling with nitric acid, and by oil of vitriol when concentrated and hot, being in this case resolved into ammonia, carbon dioxide, and carbon monoxide. Heated with concentrated solutions of caustic alkalies, it is decomposed into ammonia and oxalic acid.

Alloxan, $C_4N_2H_2O_4$. — This is the characteristic product of the action of concentrated nitric acid on uric acid in the cold. An acid is prepared of sp. gr. about 1·45, and placed in a shallow open basin: into this a third of its weight of dry uric acid is thrown, by small portions, with constant agitation, care being taken that the temperature never rises to any considerable extent. The uric acid at first dissolves, with copious effervescence of carbon dioxide and nitrogen, and eventually the whole becomes a mass of white, crystalline, pasty matter. This is left to stand some hours, drained from the acid liquid in a funnel having its neck stopped with powder and fragments of glass, and afterward more effectually dried upon a porous tile. This is *alloxan* in a crude state: it is purified by solution in a small quantity of water, and crystallization.

Alloxan crystallizes with facility from a hot and concentrated solution, slowly suffered to cool, in solid, hard, anhydrous crystals of great regularity, which are transparent, nearly colorless, have a high degree of lustre, and the figure of a modified rhombic octohedron. These crystals are monohydrated, consisting of $C_4N_2H_2O_4$. Aq. A cold solution, on the other hand, left to evaporate spontaneously, deposits large foliated crystals containing 4 molecules of water: they effloresce rapidly in the air. The monohydrate heated to 150°–160° C. (302°–320° F.) in a stream of dry hydrogen gives off its water, and leaves anhydrous alloxan, $C_4N_2H_2O_4$. Alloxan is very soluble in water: the solution has an acid reaction, a disagreeably astringent taste, and stains the skin, after a time, red or purple. It is decomposed by alkalies, and both by oxidizing and deoxidizing agents: its most characteristic property is that of forming a deep-blue compound with a ferrous salt and an alkali.

Alloxanic Acid, $C_4N_2H_4O_5$. — The barium-salt of this acid is deposited in small colorless, pearly crystals, when baryta-water is added to a solution of alloxan, heated to 60° C. (140° F.), as long as the precipitate first produced redissolves, and the filtered solution is then left to cool. The barium may be separated by the cautious addition of dilute sulphuric acid, and the filtered liquid by gentle evaporation yields alloxanic acid in small radiated needles. It has an acid taste and reaction, decomposes carbonates, and dissolves zinc with disengagement of hydrogen. It is a bibasic

acid. The alloxanates of the alkali-metals are freely soluble: those of the earth-metals dissolve in a large quantity of tepid water; that of silver is quite insoluble and anhydrous.

Mesoxalic Acid, $C_3H_2O_5$. — When a warm saturated solution of barium alloxanate is heated to ebullition, a precipitate falls, which is a mixture of barium carbonate, alloxanate, and mesoxalate: the solution is found to contain unaltered barium alloxanate and urea. Mesoxalic acid is best prepared by slowly adding solution of alloxan to a boiling-hot solution of lead acetate: the heavy granular precipitate of lead mesoxalate thus produced is washed and decomposed by sulphuretted hydrogen: urea is also formed in this reaction (p. 725). Mesoxalic acid is crystallizable: it has a sour taste and powerfully acid reaction, and resists a boiling heat: it forms sparingly soluble salts with barium and calcium, and a yellowish insoluble compound with silver, which is reduced with effervescence when gently heated.

Mycomelic Acid, $C_4N_4H_4O_2$. — This acid is formed when ammonia in excess is added to a solution of alloxan, the whole heated to ebullition, and afterward supersaturated with dilute sulphuric acid: it then separates as a yellow, light precipitate, which increases in quantity as the liquid cools. It is but feebly soluble in water, easily dissolved by alkalies, and forms a yellow silver-salt. Its formation from alloxan and ammonia is represented by the equation:

$$C_4N_2H_2O_4 + 2NH_3 = C_4N_4H_4O_2 + 2H_2O.$$

Parabanic Acid, or Paraban, $C_3N_2H_2O_3$. — This is the characteristic product of the action of moderately strong nitric acid on uric acid or alloxan, *by the aid of heat:*

$$C_5N_4H_4O_3 + O_2 + 2H_2O = C_3N_2H_2O_3 + 2CO_2 + 2NH_3.$$

It is conveniently prepared by heating together 1 part of uric acid and 8 parts of nitric acid until the reaction has nearly ceased; the liquid is evaporated to a syrupy state and left to cool; and the acid drained from the mother-liquor is purified by re-crystallization. Parabanic acid forms colorless, transparent, thin, prismatic crystals, which are permanent in the air: it is easily soluble in water, has a pure and powerfully acid taste, and reddens litmus strongly. Neutralized with ammonia, and mixed with silver nitrate, it gives a white precipitate.

Oxaluric Acid, $C_3H_2N_4O_4$. — The ammonium-salt of this acid separates in colorless needles, when a solution of parabanic acid saturated with ammonia is boiled for a moment, and then left to cool. The acid is obtained by adding an excess of dilute sulphuric acid to a hot and strong solution of the ammonium-salt, and cooling the whole rapidly. It forms a white, crystalline powder, of acid taste and reaction, capable of combining with bases: the *barium-* and *calcium-salts* are sparingly soluble; the *silver-salt* crystallizes from the mixed hot solution of silver nitrate and ammonium oxalurate in long, silky needles. Oxaluric acid contains the elements of 1 molecule of parabanic acid and 1 molecule of water. Its solution is resolved by ebullition into free oxalic acid and oxalate of urea.

Thionuric Acid, $C_4N_3H_5SO_8$. — This acid, which contains the elements of alloxan, ammonia, and sulphurous oxide ($C_4N_2H_2O_4 + NH_3 + SO_2$), is formed, as an ammonium-salt, when a cold solution of alloxan is mixed with a saturated aqueous solution of sulphurous acid, in such quantity that the odor of the gas remains quite distinct; an excess of ammonium carbonate mixed with a little caustic ammonia is then added, and the whole

boiled for a few minutes. On cooling, *ammonium thionurate* is deposited in great abundance, forming beautiful, colorless, crystalline plates, which by solution in water and re-crystallization acquire a fine pink tint. A solution of this salt gives with lead-acetate a precipitate of insoluble lead thionurate, which is at first white and gelatinous, but shortly becomes dense and crystalline: from this compound the acid may be obtained by the aid of sulphuretted hydrogen. It forms a white crystalline mass, permanent in the air, very soluble in water, of acid taste and reaction, and capable of combining directly with bases. When its solution is heated to the boiling point, it undergoes decomposition, yielding sulphuric acid and *uramile*, or *dialuramide*, $C_4N_3H_5O_3$:

$$C_4N_3H_5SO_6 + H_2O = SO_4H_2 + C_4N_3H_5O_3.$$

Uramile. — To prepare this substance, ammonium thionurate is dissolved in hot water, mixed with a small excess of hydrochloric acid, and the whole boiled in a flask: the uramile then separates as a white, crystalline substance, increasing in quantity till the contents of the vessel often become semi-solid. After cooling, it is collected on a filter, washed with cold water to remove the sulphuric acid, and dried by gentle heat, during which it frequently becomes pinkish. It is tasteless and nearly insoluble in water, but dissolves in ammonia and the fixed alkalies. The ammoniacal solution becomes purple in the air. It is decomposed by strong nitric acid, with formation of alloxan and ammonium nitrate:

$$C_4N_3H_5O_3 + O = C_4N_2H_2O_4 + NH_3.$$

Uramile, heated with aqueous solution of potassium cyanate, is converted into *pseudo-uric acid*, $C_5N_4H_6O_4 = C_4N_3H_5O_3 + CNHO$.

Uramile, added to argentic or mercuric oxide suspended in boiling water, is converted into murexide (p. 732).

Alloxantin, $C_8N_4H_4O_7 . 3\ Aq.$ — This substance is the chief product of the action of hot dilute nitric acid upon uric acid, and is likewise produced by the action of deoxidizing agents upon alloxan, anhydrous alloxantin, in fact, containing 1 atom of oxygen less than 2 molecules of alloxan. It is best prepared by passing sulphuretted hydrogen gas through a moderately strong and cold solution of alloxan. The mother-liquor from which the crystals of alloxan have separated answers the purpose perfectly well: it is diluted with a little water, and a copious stream of gas transmitted through it. Sulphur is then deposited in large quantity, mixed with a white, crystalline substance, which is the alloxantin. The product is drained upon a filter, slightly washed, and then boiled in water: the filtered solution deposits the alloxantin on cooling. Alloxantin forms small, four-sided, oblique rhombic prisms, colorless and transparent; it is soluble with difficulty in cold water, but more freely at a boiling temperature. The solution reddens litmus, gives with baryta-water a violet-colored precipitate, which disappears on heating, and when mixed with silver nitrate produces a black precipitate of metallic silver. Heated with chlorine or nitric acid, it is changed by oxidation to alloxan. The crystals become red when exposed to ammoniacal vapors. They contain 3 molecules of water, which they do not give off till heated above 150° C. (302° F.).

Alloxantin is readily decomposed: when a stream of sulphuretted hydrogen is passed through its boiling solution, sulphur is deposited and dialuric acid is produced. A hot saturated solution of alloxantin mixed with a neutral salt of ammonia instantly assumes a purple color, which, however, quickly vanishes, the liquid becoming turbid from the formation of uramile: the solution is then found to contain alloxan and free acid. With silver oxide, alloxantin gives off carbon dioxide, reduces a portion of the

metal, and converts the remainder of the oxide into oxalurate. Boiled with water and lead dioxide, alloxantin gives urea and lead carbonate.

Dialuric Acid, $C_4N_2H_4O_4$. — This acid is the final product of the action of reducing agents on alloxan, and is formed when sulphuretted hydrogen is passed through a boiling solution of alloxan till no further action takes place: $C_4N_2H_2O_4 + H_2S = C_4N_2H_4O_4 + S$. It forms colorless needles, resembling those of alloxantin, has a strong acid reaction, and neutralizes acids completely, forming salts which are sparingly soluble in water.

Hydurilic Acid, $C_8N_4H_6O_6$. — Dialuric acid, heated to about 160° C. (320° F.), with glycerin (which acts merely as a solvent), splits up into formic acid, carbon dioxide, and the ammonium-salt of *hydurilic acid:*

$$5C_4N_2H_4O_4 = CH_2O_2 + 3CO_2 + 2C_8N_4H_5(NH_4)O_6.$$

By converting this ammonium-salt into a copper-salt, and decomposing the latter with hydrochloric acid, hydurilic acid is obtained in crystals.

Hydurilic acid is converted by fuming nitric acid into *alloxan*, without any other product; but with nitric acid of ordinary strength it yields alloxan, together with *violuric acid*, *violantin*, and *dilituric acid:* *

$$\underset{\text{Hydurilic acid.}}{C_8N_4H_6O_6} + NO_3H = \underset{\text{Violuric acid.}}{C_4N_3H_3O_4} + \underset{\text{Alloxan.}}{C_4N_2H_2O_4} + H_2O$$

$$\underset{\text{Hydurilic acid.}}{C_8N_4H_6O_6} + 2NO_3H = \underset{\text{Dilituric acid.}}{C_4N_3H_3O_5} + \underset{\text{Alloxan.}}{C_4N_2H_2O_4} + NO_2H + H_2O.$$

If the action be carried on to the end, dilituric acid is the only product. This acid may indeed be regarded as a product of the oxidation of violuric acid: $C_4N_3H_3O_5 = C_4N_3H_3O_4 + O$; and violantin as a compound of the two.

Dibromobarbituric Acid, or Bromalloxan, $C_4N_2H_2Br_2O_3$, is produced, together with alloxan, by the action of bromine on hydurilic acid:

$$C_4N_4H_6O_6 + Br_6 + H_2O = C_4N_2H_2Br_2O_3 + C_4N_2H_2O_4 + 4HBr.$$

It crystallizes in colorless, shining plates, or prisms, belonging to the trimetric system, soluble in water, very soluble in alcohol and ether. By *hydrogen sulphide*, in presence of water, it is reduced to dialuric acid:

$$C_4N_2H_2Br_2O_3 + H_2S + H_2O = C_4N_2H_4O_4 + 2HBr + S.$$

With a small quantity of *hydriodic acid* it yields hydurilic acid:

$$2C_4N_2H_2Br_2O_3 + 6HI = C_8N_4H_6O_6 + 4HBr + 3I_2;$$

but when it is heated with excess of hydriodic acid, the reduction goes a step farther, and *barbituric acid*, $C_4N_2H_4O_3$, is produced:

$$C_4N_2H_2Br_2O_3 + 4HI = C_4N_2H_4O_3 + 2HBr + 2I_2.$$

Barbituric acid crystallizes in beautiful prisms, containing two molecules of water. It is bibasic, and yields chiefly acid salts, which are obtained by treating the corresponding acetates with barbituric acid.

Barbituric acid is converted by fuming nitric acid into dilituric acid, by potassium nitrate into potassium violurate. When boiled with potash it gives off ammonia, and yields the potassium-salt of *malonic acid*, $C_3H_4O_4$

* For descriptions of these several products, see Watts's Dictionary of Chemistry.

(p. 661), whence it appears to have the constitution of *malonyl urea*, $CN_2H_2(C_3H_2O_2)''O$. $C_2H_4O_4 + CN_2H_4O - 2H_2O$.

Murexide, $C_8N_6H_8O_6$. Aq.; Prout's *Purpurate of Ammonia.* — There are several methods of preparing this magnificent compound. It may be made directly from uric acid, by dissolving that substance in dilute nitric acid, evaporating to a certain point, and then adding to the warm but not boiling liquid a very slight excess of ammonia. In this process alloxantin is first produced, and is afterward partially converted into alloxan: the presence of both is requisite for the production of murexide. This process is, however, very precarious, and often fails altogether. An excellent method is to boil for a few minutes in a flask a mixture of 1 part of dry uramile, 1 part of red oxide of mercury, and 40 parts of water, to which two or three drops of ammonia have been added: the whole assumes in a short space of time an intensely deep purple tint, and when filtered boiling hot, deposits, on cooling, splendid crystals of murexide, unmixed with any impurity. The reaction in this case is:

$$\underset{\text{Uramile.}}{2C_4N_3H_5O_3} + O = \underset{\text{Murexide.}}{C_8N_6H_8O_6} + H_2O.$$

A third, and perhaps even still better process, is that of Dr. Gregory: 7 parts of alloxan and 4 parts of alloxantin are dissolved in 240 parts of boiling water, and the solution is added to about 80 parts of cold, strong solution of ammonium carbonate: the liquid instantly acquires such a depth of color as to become opaque, and gives on cooling a large quantity of murexide: the operation succeeds best on a small scale.

Murexide* crystallizes in small square prisms, which by reflected light exhibit a splendid green metallic lustre, like that of the wing-cases of the rose-beetle and other insects: by transmitted light they are deep purple-red. It is soluble with difficulty in cold water, much more easily at the boiling heat, insoluble in alcohol and ether. Mineral acids decompose it, with separation of a white or yellowish substance called *murexan*, probably identical with uramile, and caustic potash dissolves it, with production of a most magnificent purple color, which disappears when the solution is boiled.

A few years ago, murexide was extensively used in dyeing; it is now rapidly being superseded by rosaniline, the crimson derived from aniline.

A series of substances closely related to the derivatives of uric acid will be noticed under the head of Caffeine.

COMPOUND AMMONIAS or AMINES.

These names are given to a class of compounds derived from ammonia, NH_3, by substitution of alcohol-radicals for hydrogen, these radicals being either monatomic or polyatomic; the substitution may take place in one, two, or a greater number of ammonia molecules, thus giving rise to *monamines*, *diamines*, *triamines*, &c. Moreover, the nitrogen in these bases may be replaced by phosphorus, arsenic, or antimony, giving rise to phosphines, arsines, and stibines, bases analogous in composition and properties to the amines. Connected with these last-mentioned bases are certain compounds of alcohol-radicals with metals not belonging to the nitrogen class. The natural organic bases, or *alkaloïds*, found in plants, and certain artificial bases whose constitution has not been very exactly made out, will be treated in an appendix to the alcoholic ammonias.

* So called from the Tyrian dye, said to have been prepared from a species of *murex*, or shell-fish.

AMINES DERIVED FROM MONATOMIC ALCOHOLS.

Ammonia, NH_3, may give up one, two, or three of its hydrogen-atoms in exchange for univalent alcohol-radicals (methyl and its homologues, for example), producing *primary*, *secondary*, and *tertiary amines*. If A, B, C, denote three such alcohol-radicals, the amines formed by substituting them for hydrogen in ammonia will be represented by the general formulæ:

$N\{^{A}_{H}_{H}$	$N\{^{A}_{B}_{H}$	$N\{^{A}_{B}_{C}$
Primary.	Secondary.	Tertiary.

In the secondary and tertiary amines the alcohol-radicals denoted by A, B, C may be either the same or different; for example:

Secondary.		Tertiary.		
$N\{^{CH_3}_{CH_3}_{H}$	$N\{^{CH_3}_{C_2H_5}_{H}$	$N\{^{CH_3}_{CH_3}_{CH_3}$	$N\{^{CH_3}_{CH_3}_{C_2H_5}$	$N\{^{CH_3}_{C_2H_5}_{C_5H_{11}}$
Diamethyl-amine.	Methyl-ethylamine.	Trimethyl-amine.	Dimethyl-ethylamine.	Methyl-ethyl-amylamine.

It is clear that amines containing only univalent alcohol-radicals must be derived from only one molecule of ammonia: for to bind together two or more such molecules would require the introduction of a polyatomic radical: thus, $N_N\{^{H_2}_{(C_2H_4)''}_{H_2}$ is a stable compound, but such a compound as $N_N\{^{H_2}_{(C_2H_5)_2}_{H_2}$ would split up into two molecules, each consisting of $N\{^{H_2}_{C_2H_5}$.

In other words, amines derived from monatomic alcohols must be monamines.

These amines are basic compounds more or less resembling ammonia in odor, having an alkaline reaction on vegetable colors, and uniting with acids to form salts which are analogous in composition to the ammonium-salts, and, like the latter, may be regarded either as compounds of ammonia-molecules with acids, or of ammonium molecules with halogen elements and acid radicals analogous thereto (see p. 310); thus:

NH_3 Ammonia.	+ HCl	= $NH_4.Cl$	Ammonium chloride.
$NH_2(C_2H_5)$ Ethyl-ammonia.	+ HCl	= $NH_3(C_2H_5).Cl$	Ethylammonium chloride.
$NH(C_2H_5)_2$ Diethyl-ammonia.	+ HCl	= $NH_2(C_2H_5)_2.Cl$	Diethylammonium chloride.
$N(C_2H_5)_3$ Triethyl-amine.	+ HCl	= $NH(C_2H_5)_3.Cl$	Triethylammonium chloride.
$2N(C_2H_5)_3$ Triethyl-amine.	+ H_2SO_4	= $[NH(C_2H_5)_3]_2SO_4$	Triethylammonium sulphate.

All the salts of these amines, when heated with potash, give off the amine, just as ammonia-salts give off ammonia.

The tertiary amines can unite with the chlorides, &c., of alcohol-radicals in the same manner as with acids: thus triethylamine, $N(C_2H_5)_3$, unites directly with ethyl iodide, C_2H_5I, forming a compound which may be regarded either as *triethylamine ethyliodide*, $N(C_2H_5)_3 . C_2H_5I$, or as *tetrethylammonium iodide*, $N(C_2H_5)_4 . I$. Now this iodide, when heated with potash, does not give off ammonia or a volatile ammonia-base; but when heated with silver oxide and water, it is converted, by exchange of iodine for hydroxyl, into a strongly alkaline base, called *tetrethylammonium hydrate*, which may be obtained in the solid state, and exhibits reactions closely analogous to those of the fixed caustic alkalies. Its formation is represented by the equation:

$$N(C_2H_5)_4I + KOH = KI + N(C_2H_5)_4(OH).$$

Moreover, this base can exchange its hydroxyl for chlorine, bromine, and other acid radicals, just like potash or soda, forming solid crystallizable salts like the iodide above mentioned. These compounds, containing four equivalents of alcohol-radicals, are, in fact, analogous in every respect to ammonium-salts, excepting that the corresponding hydrates are capable of existing in the solid state, whereas ammonium hydrate, $NH_4(OH)$, splits up, as soon as formed, into ammonia and water. The radicals $N(C_2H_5)_4$, &c., corresponding to ammonium, are not known in the free state.

The monamines containing more than one carbon-atom are susceptible of isomeric modifications similar to those of the alcohols; thus ethylamine, $NH_2(C_2H_5)$, is isomeric with dimethylamine, $NH(C_2H_3)_2$; propylamine, $NH_2(C_3H_7)$, is isomeric with methyl-ethylamine, $NH(CH_3)(C_2H_5)$, and with trimethylamine, $N(CH_3)_3$, &c., &c., the number of possible modifications of course increasing with the complexity of the molecules. Moreover, a monamine, either primary, secondary, or tertiary, may admit of modification in the alcohol-radical itself; thus the primary monamine, $NH_2(C_3H_7)$, may exhibit the two following modifications:

$N\begin{cases}CH_2CH_2CH_3\\H\\H\end{cases}$ Propylamine.

$N\begin{cases}CH(CH_3)_2\\H\\H\end{cases}$ Isopropylamine.

An instance of isomerism of this latter kind has lately been observed by Wurtz in amylamine, $NH_2(C_5H_{11})$.

Amines may of course be formulated on the methane or marsh-gas type instead of the ammonia type, the radical amidogen, NH_2, and others derived from it, being substituted for an atom of hydrogen; thus:

$C\begin{cases}H\\H\\H\\H\end{cases}$ Methane. $C\begin{cases}H\\H\\H\\NH_2\end{cases}$ Methyl-amine. $C\begin{cases}CH_3\\H\\H\\NH_2\end{cases}$ Ethyl-amine. $C\begin{cases}H\\H\\H\\NH(CH_3)\end{cases}$ Dimethyl-amine. $C\begin{cases}H\\H\\H\\N(CH_3)_2\end{cases}$ Trimethyl-amine.

This mode of representation is convenient in some cases, but the amines and their salts are so closely related to the ammonia-compounds in their modes of formation and transformation, that they are for the most part more appropriately represented by formulæ derived from ammonia, NH_3, and sal-ammoniac, NH_4Cl.

A great number of amines and their salts have been obtained, but the limits of this work will not allow us to describe more than the most impor-

tant of those containing the radicals, methyl, ethyl, amyl, and phenyl. In describing them it will be convenient to make a slight departure from the natural order, and commence with the ethyl bases, which have been more completely studied than their homologues.

BASES OF THE ETHYL SERIES.

Ethylamine, or Ethyl-ammonia, $C_2H_7N = NH_2(C_2H_5)$. — On digesting ethyl bromide or iodide with an alcoholic solution of ammonia, the alkaline reaction of the ammonia gradually disappears; and on evaporating the solution on the water-bath, a white crystalline mass is obtained, which consists chiefly of ethyl-ammonium bromide or iodide: $NH_3 + C_2H_5I = NH_3(C_2H_5)I$. On distilling this salt in a retort provided with a good condenser, with caustic lime, the ethylamine is liberated and distils over:

$$2NH_3(C_2H_5)I + CaO = 2NH_2(C_2H_5) + H_2O\ CaI_2.$$

Another method of preparing this compound, and, indeed, the method by which it was first obtained by Wurtz, consists in submitting ethyl cyanate to the action of potassium hydrate. Cyanic acid (p. 710), when treated with boiling solution of potash, splits into carbon dioxide and ammonia; and ethyl cyanate (p. 714) suffers a perfectly analogous decomposition, yielding carbon dioxide and ethylamine:

$CNHO$	+	$2KHO$	=	K_2CO_3	+	NH_3
Cyanic acid.						Ammonia.
$CN(C_2H_5)O$	+	$2KHO$	=	K_2CO_3	+	$NH_2(C_2H_5)$
Ethyl cyanate.						Ethylamine.

Ethyl cyanurate, polymeric with the cyanate, likewise gives off ethylamine when boiled with potash.

Ethylamine is a very mobile liquid, of sp. gr. 0·6964, at 8° C. (46° F.), boiling at 19° C. (66° F.). The specific gravity of its vapor is 1·57. It has a most powerful ammoniacal odor, and restores the blue color to reddened litmus-paper. It produces white clouds with hydrochloric acid, and is absorbed by water with great avidity. With acids it forms a series of neutral crystallizable salts perfectly analogous to those of ammonium.

Ethylamine imitates, moreover, in a remarkable manner, the deportment of ammonia with metallic salts. It precipitates the salts of magnesium, aluminium, iron, manganese, bismuth, chromium, uranium, tin, lead, and mercury; zinc-salts yield a white precipitate, which is soluble in excess. Like ammonia, ethylamine dissolves silver chloride, and yields with copper-salts a blue precipitate, which is soluble in an excess of ethylamine. On adding ethylamine to oxalic ether, a white precipitate of *biethyl-oxamide*, $N_2(C_2O_2)''H_2(C_2H_5)_2$, is produced: a compound analogous to oxamic acid (p. 659) has also been obtained. Ethylamine may, however, be readily distinguished from ammonia: its vapor is inflammable, and it produces with platinic chloride, a salt, $[NH_3(C_2H_5)Cl]_2PtCl_4$, crystallizing in golden scales, which are rather soluble in water. Treated with chlorine, it yields ethyl-ammonium chloride and *bichlorethylamine*, $NCl_2C_2H_5$, a yellow liquid having a penetrating, tear-exciting odor. When treated with potash, it is converted into ammonia, potassium acetate, and potassium chloride: $NCl_2(C_2H_5) + 3KHO = C_2H_3KO_2 + 2KCl + NH_3 + H_2O$.

Ethyl-urea. — On passing the vapor of cyanic acid into a solution of ethylamine, the liquid becomes hot, and deposits, after evaporation, fine

crystals of ethyl-urea: $C_2H_7N + CNHO = C_3H_8N_2O = CH_3(C_2H_5)N_2O$. This substance, which may be viewed as ordinary urea (p. 721), having 1 atom of hydrogen replaced by ethyl, may also be prepared by treating cyanic ether with ammonia: $CN(C_2H_5)O + NH_3 = C_3H_8N_2O$. Ethyl-urea is very soluble in water and alcohol: the concentrated aqueous solution, unlike that of ordinary urea, yields no precipitate with nitric acid; but on gently evaporating the mixture, a very soluble crystalline nitrate of ethyl-urea is obtained. Boiled with potash, this substance yields a mixture of equivalent quantities of ammonia and ethylamine: $C_3H_8N_2O + 2KHO = K_2CO_3 + NH_3 + C_2H_7N$.

Biethylamine, $C_4H_{11}N = NH(C_2H_5)_2$. — A mixture of the solutions of ethylamine and ethyl bromide, heated in a sealed tube for several hours, solidifies to a crystalline mass of biethyl-ammonium bromide: $NH_2C_2H_5 + C_2H_5Br = NH_2(C_2H_5)_2Br$. This bromide, distilled with potash, yields biethylamine as a colorless liquid, still very alkaline, and soluble in water, but less so than ethylamine. This compound boils at 57·5° C. (135° F.). It forms beautifully crystallizable salts with acids. A solution of biethyl-ammonium chloride forms with platinic chloride a very soluble double salt, $2NH_2(C_2H_5)_2Cl \cdot PtCl_4$, crystallizing in orange-red grains, very different from the orange-yellow leaves of the corresponding ethyl-ammonium salt.

Biethyl-urea. — Biethylamine behaves with cyanic acid like ammonia and ethylamine, giving rise to biethyl-urea. A substance similar to, but not identical with, the former, has been produced by the action of cyanic ether upon ethylamine: $CN(C_2H_5)O + C_2H_7N = C_5H_{12}N_2O = C[H_2(C_2H_5)_2]N_2O$. The biethyl-ureas are very crystallizable, and readily form crystalline nitrates. Boiled with potash, the biethyl-ureas yield, the former 1 molecule of biethylamine and 1 molecule of ammonia, $C[H_2(C_2H_5)_2]N_2O + 2KHO = K_2CO_3 + NH(C_2H_5)_2 + NH_3$; the latter, pure ethylamine, $C[H_2(C_2H_5)_2]N_2O + 2KHO = K_2CO_3 + 2NH_2(C_2H_5)$.

Triethylamine, $C_6H_{15}N = N(C_2H_5)_3$. — The formation of this body is perfectly analogous to that of ethylamine and of biethylamine. On heating for a short time a mixture of biethylamine with ethyl bromide in a sealed glass tube, a beautiful fibrous mass of triethyl-ammonium bromide is obtained, from which the triethylamine may be separated by potash. Triethylamine is a colorless, powerfully alkaline liquid, boiling at 91° C. (196° F.). The salts of this base crystallize remarkably well. With platinic chloride it forms a very soluble double salt, $2NH(C_2H_5)_3Cl \cdot PtCl_4$, which crystallizes in magnificent, large, orange-red rhombs.

The action of ethyl iodide or bromide on ammonia gives rise to the simultaneous formation of the three ethylated bases, which, though differing considerably in their boiling points, can scarcely be separated by fractional distillation. The separation succeeds, however, by digesting the mixture of these three bases with anhydrous ethyl oxalate. Ethylamine is thus converted into diethyloxamine:

$$\underset{\text{Ethyl oxalate.}}{C_2O_4(C_2H_5)_2} + \underset{\text{Ethyl-amine.}}{2NH_2(C_2H_5)} = \underset{\text{Alcohol.}}{2C_2H_5(OH)} + \underset{\text{Diethyl-oxamide.}}{N_2(C_2O_2)''H_2(C_2H_5)_2}$$

and diethylamine forms diethyloxamate:

$$\underset{\text{Ethyl oxalate.}}{C_2O_4(C_2H_5)_2} + \underset{\text{Diethyl-amine.}}{NH(C_2H_5)_2} = \underset{\text{Alcohol.}}{C_2H_5(OH)} + \underset{\text{Ethylic diethyloxamate;}}{C_2O_2[N(C_2H_5)_2](OC_2H_5)}$$

whereas triethylamine does not combine with oxalic ether. The separation is carried out in the following manner:

On distilling the product of the reaction of ethyl oxalate upon the mix-

ture of ethyl bases in the water-bath, pure triethylamine passes over; and on treating the residue with boiling water, diethyloxamide is dissolved, while ethyl diethyloxamate remains as an insoluble layer floating upon the hot solution: it may be separated by a tap-funnel. Diethyloxamide treated with potash yields pure ethylamine, while pure diethylamine is obtained by treating ethylic diethyloxamate with the same reagent.

Tetrethyl-ammonium Hydrate, $C_8H_{21}NO = N(C_2H_5)_4(OH)$. — When anhydrous triethylamine is mixed with dry ethyl iodide, a powerful reaction ensues, the mixture enters into ebullition, and solidifies on cooling to a white crystalline mass of tetrethyl-ammonium iodide: $N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$. This iodide is readily soluble in hot water, from which it crystallizes on cooling in beautiful crystals of considerable size. This substance is not decomposed by potash: it may be boiled with the alkali for hours without yielding a trace of volatile base. The iodine may, however, be readily removed by treating the solution with silver-salts. If in this case silver sulphate or nitrate be used, we obtain, together with silver iodide, the sulphate or nitrate of tetrethyl-ammonium, which crystallizes on evaporation: on the other hand, if the iodide be treated with freshly precipitated silver oxide, the hydrate of tetrethyl-ammonium itself is separated. On filtering off the silver precipitate, a clear colorless liquid is obtained, which contains the isolated base in solution. It has a strongly alkaline reaction, and intensely bitter taste. The solution of tetrethyl-ammonium hydrate has a remarkable analogy to potash and soda. Like these substances, it destroys the epidermis and saponifies fatty substances, with formation of true soaps. With metallic salts it exhibits exactly the same reactions as potash. On evaporating a solution of the base in a vacuum, long slender needles are deposited, which are evidently the hydrate with an additional amount of crystallization water. After some time these needles disappear again, and a semi-solid mass is left, which is the hydrate of tetrethyl-ammonium. A concentrated solution of this substance in water may be boiled without decomposition, but on heating the dry substance, it is decomposed into pure triethylamine, water, and olefiant gas:

$$N(C_2H_5)_4(OH) = H_2O + N(C_2H_5)_3 + C_2H_4.$$

Tetrethyl-ammonium hydrate forms neutral salts with acids. These salts are mostly very soluble; several yield beautiful crystals. The platinum-salt, $2N(C_2H_5)_4Cl \cdot PtCl_4$, forms orange-yellow octohedrons, which are about as soluble as the corresponding potassio-platinic salt.

BASES OF THE METHYL SERIES.

Methylamine, $CH_5N = NH_2(CH_3)$. — The formation and the method of preparing this compound from methyl cyanate are perfectly analogous to those of ethylamine (p. 735): however, methylamine being a gas at the common temperature, it is necessary to cool the receiver by a freezing mixture. The distillate, which is an aqueous solution of methylamine, is saturated with hydrochloric acid, and evaporated to dryness. A crystalline residue is thus obtained, consisting of methylammonium chloride, and this, when distilled with dry lime, yields methylamine gas, which, like ammonia gas, must be collected over mercury. It is distinguished from ammonia by a slightly fishy odor, and by the facility with which it burns. Methylamine is liquefied at about —18°: its sp. gr. is 1·08. This substance is the most soluble of all gases; at 12° C. (54° F.), one volume of water absorbs 1040

volumes of the gas. It is likewise very readily absorbed by charcoal. In its chemical deportment with acids and other substances, methylamine resembles in every respect ammonia and ethylamine. Methylamine appears to be produced in a great number of processes of destructive distillation: it has been formed by distilling several of the natural organic bases, such as codeine, morphine, caffeine, and several others, with caustic potash; frequently a mixture of several bases is produced in this manner.

Among the numerous derivatives already obtained with this substance, *methyl-urea*, $CH_3(CH_3)N_2O$, *bimethyl-urea*, $CH_2(CH_3)_2N_2O$, and *methyl-ethyl-urea*, $CH_2(CH_3)(C_2H_5)N_2O$, may be mentioned. The latter substance has been produced by the action of ethyl cyanate upon methylamine. A series of platinum-bases, analogous to those produced by the action of ammonia upon platinous chloride (p. 426), have likewise been obtained with methylamine.

Bimethylamine, $C_2H_7N=NH(CH_3)_2$. — This compound, isomeric with ethylamine, is prepared by the action of ammonia on methyl iodide. Its separation from the methylamine and trimethylamine simultaneously formed, is accomplished by means of oxalic ether (p. 735).

Trimethylamine, $C_3H_9N = N(CH_3)_3$. — This substance is readily obtained in a state of perfect purity, by submitting tetramethyl-ammonium hydrate to the action of heat. It is gaseous at the common temperature, but liquefies at about 90° C. (194° F.), to a mobile liquid of very powerfully alkaline reaction. Trimethylamine produces very soluble salts with acids. The platinum-salt, $2NH(CH_3)_3Cl \cdot PtCl_4$, is likewise very soluble, and crystallizes in splendid orange-red octohedrons. According to Mr. Winkles, large quantities of trimethylamine are found in the liquor in which salt herrings are preserved.

Tetramethyl-ammonium Hydrate, $C_4H_{13}NO = N(CH_3)_4(OH)$.—The corresponding iodide may be obtained by adding methyl iodide to trimethylamine. The two substances unite with a sort of explosion. The same iodide is prepared, however, with less difficulty, simply by digesting methyl iodide with an alcoholic solution of ammonia. In this reaction a mixture of the iodides of ammonium, methyl-ammonium, bimethyl-ammonium, trimethyl-ammonium, and tetramethyl-ammonium is produced. The first and last compounds are formed in largest quantity, and may be separated by crystallization, the iodide of tetramethyl-ammonium being but sparingly soluble in water. From the iodide the base itself is separated by means of silver oxide. Its properties are similar to those of the corresponding ethyl-compound. It differs, however, from tetrethyl-ammonium hydrate in its behavior when heated (p. 737), yielding trimethylamine and pure methyl alcohol, $N(CH_3)_4OH=N(CH_3)_3+CH_3(OH)$.

BASES OF THE AMYL SERIES.

The formation of these bodies being perfectly analogous to that of the corresponding terms in the ethyl series, we refer to the fuller statement given on page 735, and confine ourselves to a brief description of their principal properties.

Amylamine, $C_5H_{13}N = NH_2(C_5H_{11})$, is a colorless liquid of peculiar, penetrating, aromatic odor, slightly soluble in water, to which it imparts a strong alkaline reaction. With the acids it forms crystalline salts, which have a fatty lustre. Amylamine boils at 93° C. (199° F.).

An *amylamine-urea* has been prepared.

Biamylamine, $C_{10}H_{23}N = NH(C_5H_{11})_2$.—An aromatic liquid, less soluble in water, and less alkaline than amylamine. It boils at about 170° C. (338° F.).

Triamylamine, $C_{15}H_{33}N = N(C_5H_{11})_3$. — A colorless liquid, of properties similar to those of the two preceding bases, but boiling at 257° C. (495° F.). The salts of triamylamine are very sparingly soluble in water, and fuse, when heated, to colorless liquids, floating upon water.

Tetramyl-ammonium Hydrate, $C_{20}H_{45}NO = N(C_5H_{11})_4OH$. — This substance is far less soluble than the corresponding bases of the methyl and ethyl series, and separates as an oily layer on adding potash to the aqueous solution. On evaporating the solution in an atmosphere free from carbonic acid, the alkali may be obtained in splendid crystals of considerable size. When submitted to distillation, it splits into water, triamylamine, and amylene:

$$N(C_5H_{11})_4OH = H_2O + N(C_5H_{11})_3 + C_5H_{10}.$$

In addition to the bases already enumerated, the following have been obtained by analogous processes, viz., treatment of the iodides of the corresponding alcohol-radicals with ammonia: propylamine, C_3H_9N, hexalamine, $C_6H_{15}N$, heptylamine, $C_7H_{17}N$, octylamine, $C_8H_{19}N$, and nonylamine, $C_9H_{21}N$.

BASES OF THE AROMATIC SERIES.

In speaking of the aromatic hydrocarbons, we have explained that each of the hydrocarbons homologous with benzene may be regarded as a compound of phenyl with one or more alcohol-radicals of the methyl series, and may give rise to two series of derivatives, accordingly as the hydrogen in the phenyl or in the alcohol-radical is replaced: thus from toluene or methyl-phenyl, $C_6H_5 . CH_3$, are derived chlorotoluene, $C_6H_4Cl . CH_3$, isomeric with benzyl chloride, $C_6H_5 . CH_2Cl$, — and cresol, $C_6H_4OH . CH_3$, isomeric with benzyl alcohol, $C_6H_5 . CH_2OH$. Each of these hydrocarbons can in like manner yield two isomeric bases, accordingly as an atom of hydrogen in one part or the other of its molecule is replaced by amidogen, NH_2: thus from toluene are derived two bases containing C_7H_9N, viz.:

$C_6H_4(NH_2) . CH_3$	$C_6H_5 . CH_2NH_2$
Toluidine.	Benzylamine.

The second of these, benzylamine, is analogous in its mode of formation, and all its principal characters, to the bases of the methyl series, and may be represented by the formula $NH_2(C_7H_7)$, derived from ammonia by substitution of the univalent radical, benzyl, C_7H_7, for hydrogen. But toluidine is formed in a different manner, viz., by the action of reducing agents on nitrotoluene, and differs in its chemical relations from benzylamine, much in the same manner as cresol from benzyl alcohol, being altogether a less active substance.

Xylidine, $C_8H_{11}N = C_6H_3(NH_2) . (CH_3)_2$; cumidine, $C_9H_{13}N = C_6H_4(NH_2) . C_3H_7$, and cymidine, $C_{10}H_{15}N$, bases homologous with toluidine, are obtained in like manner from the nitro-derivatives of the corresponding hydrocarbons. The corresponding bases homologous with benzylamine have not yet been obtained.

Aniline, C_6H_7N. — There is but one aromatic monamine containing *six* atoms of carbon, viz., aniline, C_6H_7N; and this may be regarded indifferently, either as *amidobenzene*, $C_6H_5(NH_2)$, or as *phenylamine*, $N\left\{\begin{matrix}H_2\\C_6H_5\end{matrix}\right.$, that

is to say, as a lower homologue either of toluidine or benzylamine. The two formulæ just given are in fact identical; and moreover aniline, both in its modes of formation and in its properties, exhibits resemblances, on the one hand to toluidine and its homologues, and on the other to benzylamine and the monamines of the methylic series.

Aniline is produced: 1. By heating phenol with ammonia in sealed tubes:

$$C_6H_5(OH) + NH_3 = H_2O + NH_2(C_6H_5).$$

2. By the action of hydrogen sulphide and other reducing agents on nitrobenzene:

$$C_6H_5(NO_2) + 3H_2S = 2H_2O + S_3 + C_6H_5(NH_2).$$

The first of these reactions exhibits the relation of aniline to benzylamine: the second, its relation to toluidine. — 3. By the action of caustic potash upon indigo:

$$\underset{\text{Indigo.}}{C_8H_5NO} + 4KHO + H_2O = \underset{\text{Aniline.}}{C_6H_7N} = 2CO_3K_2 + 2H_2.$$

The name aniline indicates the relation of this compound to the indigo group, the botanical name of the indigo-plant being *Indigofera anil.*

Preparation. — 1. From indigo. — Powdered indigo boiled with a highly concentrated solution of potassium hydrate dissolves, with evolution of hydrogen, to a brownish-red liquid containing anthranilic acid. If this matter be transferred to a retort and still further heated, it swells up and gives off aniline, which condenses in the form of oily drops in the neck of the retort and in the receiver. Separated from the ammoniacal water by which it is accompanied, and redistilled, it is obtained nearly colorless.

2. In order to prepare aniline from nitrobenzene (see p. 495), this substance is submitted to a process discovered by Zinin, which has proved a very abundant source of artificial organic bases. An alcoholic solution of nitrobenzene is treated with ammonia and sulphuretted hydrogen, until after some hours a precipitation of sulphur takes place. The brown liquid is now again saturated with sulphuretted hydrogen, and the process repeated until sulphur is no longer separated. The reaction may be remarkably accelerated by occasionally heating or distilling the mixture. The liquid is then mixed with excess of acid, filtered, boiled to expel alcohol and unaltered nitrobenzene, and then distilled with excess of caustic potash.

If the aniline be required quite pure, it must be converted into oxalate, the salt several times crystallized from alcohol, and again decomposed by potash.

Béchamp has shown that the reduction of nitrobenzene may be effected even more conveniently by the action of ferrous acetate. The distillation of one part of nitrobenzene, one part of acetic acid, and one and a half part of iron filings, seems, in fact, to be the best process for preparing aniline.* The mass swells violently, and very capacious retorts are required.

Aniline exists among the products of the distillation of coal, and probably of other organic matters: it is formed in the distillation of anthranilic acid, and occasionally in other reactions.

Aniline, when pure, forms a thin, oily, colorless liquid, of faint vinous odor, and aromatic, burning taste. It is very volatile, but has, nevertheless, a high boiling point (182°C. [260° F.]). In the air it gradually becomes yellow or brown, and acquires a resinous consistence. Its density is 1·028. Water dissolves aniline to a certain extent, and also forms with it a kind of hydrate: alcohol and ether are miscible with it in all proportions. It is

* According to Scheurer-Kestner, the treatment of nitrobenzene with a very large quantity of iron filings and acetic acid reproduces benzene and ammonia.

destitute of alkaline reaction to test-paper, but is quite remarkable for the number and beauty of the crystallizable compounds which it forms with acids. Two extraordinary reactions characterize this body and distinguish it from all others — viz., that with chromic acid, and that with solution of calcium hypochlorite. The former gives with aniline a deep-greenish or bluish-black precipitate, and the latter an extremely beautiful violet-colored compound, the fine tint of which is, however, very soon destroyed. When nitrous acid is passed into aniline, or when aniline hydrochloride is treated with silver nitrate, water and phenol are produced, and nitrogen is evolved:

$$C_6H_7N + NO_2H = C_6H_6O + H_2O + N_2.$$

On the other hand, when nitrous acid is passed through an alcoholic solution of aniline, 2 molecules of aniline are linked together, 3 atoms of the hydrogen being replaced by 1 atom of nitrogen. Azodiphenyldiamine, the substance thus produced, contains $C_{12}H_{11}N_3$. The following equation represents its formation:

$$2C_6H_7N + NO_2H = C_{12}H_{11}N_3 + 2H_2O.$$

By treatment of azodiphenyldiamine with nitrous acid, the same change is repeated once more, three additional atoms of hydrogen being again replaced by one of nitrogen, whereby a new substance, $C_{12}H_8N_4$, is formed according to the equation:

$$C_{12}H_{11}N_3 + NO_2H = C_{12}H_8N_4 + 2H_2O.$$

This body is remarkable for the violence with which, like fulminate of silver, it explodes. Griess, who discovered these substances, has succeeded in obtaining similar compounds from several others of the basic derivatives of aniline.

Paraniline. — In the manufacture of aniline upon a large scale, several bases, having much higher boiling points than aniline, are formed; among them there is a beautifully crystalline compound called paraniline, polymeric with aniline and represented by the formula $C_{12}H_{14}N_2 = 2C_6H_7N$. It forms two series of salts, of which the hydrochlorides, $C_{12}H_{14}N_2 . HCl$ and $C_{12}H_{14}N_2 . 2HCl$, may be quoted as examples.

Substitution-products of Aniline.

Under the head of indigo, a product of oxidation of this substance will be noticed, to which the name *isatin* has been given. When isatin is distilled with an exceedingly concentrated solution of caustic potash, it is, like indigo, resolved into aniline, carbon dioxide, and free hydrogen. In like manner, *chlorisatin* and *dichlorisatin*, similarly treated, yield products analogous to aniline, but containing one or two atoms of chlorine respectively in the place of hydrogen. The *chloraniline*, C_6H_6ClN, and *dichloraniline*, $C_6H_5Cl_2N$, thus produced, cannot, however, be obtained by the direct action of chlorine upon aniline, thus differing from ordinary substitution-compounds; but aniline may be reproduced from them by the same reagent that is capable of reconverting chloracetic acid into ordinary acetic acid — namely, an amalgam of potassium or sodium (see p. 613). They are the first cases on record of organic bases containing chlorine.

Chloraniline forms large, colorless octohedrons, having exactly the odor and taste of aniline, very volatile, and easily fusible: it distils without decomposition at a high temperature, and burns, when strongly heated, with a red smoky flame with greenish border. It is heavier than water, indifferent to vegetable colors, and, except in being solid at common temperatures, resembles aniline in the closest manner. It forms numerous and

beautiful crystallizable salts. If aniline be treated with chlorine gas, the action goes further, *trichloraniline*, $C_6H_4Cl_3N$, being produced, a volatile crystalline body which has no longer any basic properties. The corresponding bromine compounds have also been formed and described.

Nitraniline, $C_6H_5(NO_2)N$. — This compound is formed by the action of ammonium sulphide on dinitrobenzene, $C_6H_4(NO_2)_2$ (p. 495). The attempts to prepare it directly from aniline by means of nitric acid were unsuccessful, the principal product being usually picric acid. It forms yellow, acicular crystals, but little soluble in cold water, although easily dissolved by alcohol and ether. When warmed it exhales an aromatic odor, and melts. At a higher temperature it distils unchanged. By very gentle heat it may be sublimed without fusion. It is heavier than water, does not affect test-paper, and like chlor- and brom-aniline fails to give with calcium hypochlorite the characteristic reaction of the normal compound. Nitraniline forms crystallizable salts, of which the hydrochloride is the best known.

Diphenylamine, $NH(C_6H_5)_2$, is produced by the distillation of triphenylrosaniline (aniline blue). It is a crystalline body, melting at 45° C. (113° F.) to a yellow oil, which boils constantly at 310° C. (590° F.). A substance possessing the composition of *triphenylamine*, $C_{18}H_{15}N$, but probably not connected with the phenyl series, is formed by submitting the compound produced by the action of cinnamic aldehyde upon ammonium sulphite to destructive distillation, together with an excess of lime.

Cyananiline is formed by the action of cyanogen upon aniline: it is a crystalline substance capable of combining with acids like aniline, but very prone to decomposition. It contains $C_{14}H_{14}N_2 = (C_6H_7N)_2 . Cy_2$, and is therefore a compound of cyanogen with aniline, not a substitution-derivative.

Derivatives of Aniline containing Alcohol-radicals.—By treating aniline with iodide or bromide of methyl, ethyl, &c., in different proportions, bases are obtained in which the hydrogen of the aniline is more or less replaced by those radicals. *Ethylaniline*, $C_6H_6(C_2H_5)N$, or $NH(C_2H_5)(C_6H_5)$, and *diethylaniline*, $N(C_2H_5)_2(C_6H_5)$, are liquids greatly resembling aniline; the former boils at 204° C. (399° F.); the latter at 213·5° C. (416° F.). Ethylaniline treated with amyl iodide yields the *hydriodide of ethyl-amyl-aniline*, $N(C_2H_5)(C_5H_{11})(C_6H_5) . HI$, or *iodide of ethyl-amyl-phenylammonium*, $NH(C_2H_5)(C_5H_{11})(C_6H_5)I$, from which the ethyl-amyl-aniline may be separated by distillation with potash. It is an aromatic oil boiling at 262° C. (504° F.). When treated with methyl iodide, it is converted into *iodide of methyl-ethyl-amyl-phenylammonium*, $N(CH_3)(C_2H_5)(C_5H_{11})(C_6H_5)I$, from which the corresponding hydrate, $N(CH_3)(C_2H_5)(C_5H_{11})(C_6H_5) . OH$, may be obtained by treatment with silver oxide and water. This hydrate is very soluble in water, powerfully alkaline, and has an extremely bitter taste.

Many other substitution-derivatives of aniline may be obtained in a similar manner.

Toluidine, C_7H_9N, or **Amidotoluene**, $C_7H_7(NH_2) = C_6H_4(NH_2) . CH_3$.—This base is homologous with aniline, and is obtained, similarly to the latter, by the action of hydrogen sulphide or ferrous acetate on nitrotoluene, $C_7H_7(NO_2)$. It forms colorless platy crystals, very sparingly soluble in water, easily in alcohol, ether, and oils: it is heavier than water, has an aromatic taste and odor, and a very feeble alkaline reaction. At 40° C. (104° F.) it melts, and at 205°–206° C. (402° F.), boils and distils unchanged. It forms well-crystallized salts, but is nevertheless a weak base, and, according to Wanklyn, is absolutely incapable of neutralizing dilute sulphuric acid. It forms substitution-derivatives similar to those of aniline; those containing methyl and its homologues are more basic than toluidine itself.

Benzylamine, $C_6H_5 . CH_2(NH_2)$ or $NH_2(C_7H_7)$.—This compound, isomeric with toluidine, is obtained, together with dibenzylamine, $NH(C_7H_7)_2$, and tribenzylamine, $N(C_7H_7)_3$, by the action of alcoholic ammonia on benzyl chloride, $C_6H_5 . CH_2Cl$ (p. 496), the mode of formation of these bases being exactly analogous to that of methylamine and its homologues, and altogether different from that of toluidine.

Benzylamine is a colorless liquid, boiling at 182°–183° C. (360° F.) (23° C. (73° F.) lower than toluidine). It mixes in all proportions with water, and is separated therefrom by potash. It is a much stronger base than toluidine; absorbs carbon dioxide rapidly, forming a crystalline carbonate; unites readily with other acids, producing rise of temperature; and fumes with hydrochloric acid. The hydrochloride crystallizes in striated tables; the platinochloride, $2NH_3(C_7H_7)Cl . PtCl_4$, in orange-colored laminæ.

Xylidine, $C_8H_{11}N = C_6H_3(NH_2) . (CH_3)_2$, *Cumidine*, $C_9H_{13}N$, or probably $C_6H_4(NH_2) . C_3H_7$, and *Cymidine*, $C_{10}H_{15}N$, or $C_{10}H_{13}(NH_2)$, homologous with toluidine, are obtained in like manner by reduction of the corresponding nitro-derivatives. Xylidine boils at 214°–216° C. (417°–420° F.); cumidine at 225° C. (437° F.); cymidine at 250° C. (482° F.). Xylidine and cumidine form well-crystallized salts.

The isomers of these three bases, homologous with benzylamine, have not yet been obtained.

Naphthalidine, $C_{10}H_9N=C_{10}H_7(NH_2)$, is interesting, as being one of the first compounds of its kind produced by Zinin's process. It is obtained by the action of ammonium sulphide upon an alcoholic solution of *nitro-naphthalene*, one of the numerous products of the action of nitric acid upon *naphthalene*, $C_{10}H_8$. When pure it forms colorless silky needles, fusible, and volatile without decomposition. It has a powerful, not disagreeable odor, and burning taste, is nearly insoluble in water, but dissolves readily in alcohol and ether; the solution has an alkaline reaction. Naphthalidine forms numerous crystalline salts.

DIAMINES and TRIAMINES.

These are bases derived from two or three molecules of ammonia, N_2H_6 and N_3H_9, by substitution of bivalent and trivalent alcohol-radicals for a part or the whole of the hydrogen. A portion of the hydrogen may at the same time be replaced by univalent alcohol-radicals. Diamines are formed by the action of the chlorides, bromides, and iodides of the diatomic alcohol-radicals on ammonia. The examination of these compounds is far from being complete.

Ethene-diamine and Diethene-diamine.—The action of ammonia upon ethene dibromide is very complex; but among the products of the reaction there are invariably present the hydrobromides of two bases which are derived from two molecules of ammonia, viz., ethene-diamine, $C_2H_8N_2 = N_2(C_2H_4)''H_4$, an oily liquid boiling at 117° C. (242° F.), and diethene-diamine, $C_4H_{10}N_2 = N_2(C_2H_4)''_2H_2$, a crystalline solid, boiling at a high temperature. The formation of these bodies, which saturate two equivalents of acid, may be represented by the following equations:

$$2NH_3 + (C_2H_4)''Br_2 = [N_2(C_2H_4)''H_6]''Br_2, \text{ and}$$
$$4NH_3 + 2(C_2H_4)''Br_2 = [N_2(C_2H_4)''_2H_4]''Br_2 + 2NH_4Br.$$

Distillation with potash separates the bases from these salts, potassium bromide being formed at the same time.

By the action of ethyl iodide upon ethene-diamine and diethene-diamine, two series of ethylated derivatives have been obtained. We can here give only the names and formulæ of the iodides:

Bases derived from Ethene-diamine.

Iodide of Ethene-diammonium . . .	$[N_2H_6(C_2H_4)''']''I_2$.
Iodide of Diethyl-ethene-diammonium.	$[N_2H_4(C_2H_4)'''(C_2H_5)_2]''I_2$.
Iodide of Tetrethyl-ethene-diammonium	$[N_2H_2(C_2H_4)'''(C_2H_5)_4]''I_2$.
Iodide of Pentethyl-ethene-diammonium	$[N_2H(C_2H_4)'''(C_2H_5)_5]''I_2$.
Iodide of Hexethyl-ethene-diammonium	$[N_2(C_2H_4)'''(C_2H_5)_6]''I_2$.

Bases derived from Diethene-diamine.

Iodide of Diethene-diammonium . . .	$[N_2H_4(C_2H_4)''_2]''I_2$.
Iodide of Diethyl-diethene-diammonium	$[N_2H_2(C_2H_4)''_2(C_2H_5)_2]''I_2$.
Iodide of Triethyl-diethene-diammonium	$[N_2H(C_2H_4)''_2(C_2H_5)_3]''I_2$.
Iodide of Tetrethyl-diethene-diammonium	$[N_2(CN_2H_4)''_2(C_2H_5)_4]''I_2$.

DIETHENE-TRIAMINE AND TRIETHENE-TRIAMINE. — More recently two other bases have been separated from the product of the action of ethene dibromide upon ammonia, viz., diethene triamine, $(C_2H_4)_2H_5N_3$. and triethene-triamine, $(C_2H_4)_3H_3N_3$. The formation of these bodies, which saturate 3 equivalents of acid, may be represented by the following equations:

$$4NH_3 + 2(C_2H_4)''Br_2 = [N_3(C_2H_4)''_2H_8]'''Br_3 + NH_4Br$$
$$6NH_3 + 3(C_2H_4)''Br_2 = [N_3(C_2H_4)''_3H_6]'''Br_3 + 3NH_4Br.$$

DIPHENYL-ETHENE-DIAMINE, $N_2H_2(C_2H_4)''(C_6H_5)_2$, and DIPHENYL-DIETHENE-DIAMINE, $N_2(C_2H_4)''_2(C_6H_5)_2$. — Aniline, when submitted to the action of ethene bromide, $C_2H_4Br_2$, solidifies to a crystalline mass, from which potash separates two crystalline bases, which are soluble in alcohol and in ether, but insoluble in water. If a large quantity of ethene bromide be made to act upon a comparatively small quantity of aniline, the new salt contains the hydrobromide of diphenyl-ethene-diamine, or ethene-dianaline, $C_{14}H_{16}N_2 . 2HBr = 2C_6H_7N + C_2H_4Br_2$. On the other hand, if the aniline be employed in excess, hydrobromide of diethene-dianiline, or diphenyl-diethene-diamine, $C_{16}H_{18}N_2 . 2HBr$, is formed, together with hydrobromide of aniline: $4C_6H_7N + 2C_2H_4Br_2 = C_{16}H_{18}N_2 . 2HBr + 2(C_6H_7N . HBr)$.

METHENYL-DIPHENYL-DIAMINE, $C_{13}H_{12}N_2 = N_2H(CH)'''(C_6H_5)_2$, also called *Formyl-aniline.* — A mixture of aniline and chloroform exposed in sealed tubes to a temperature of 180° solidifies to a crystalline mass, consisting of aniline hydrochloride and the hydrochloride of methenyl-diphenyl-diamine:

$$4C_6H_7N + CHCl_3 = 2(C_6H_7N . HCl) + C_{13}H_{12}N_2 . HCl.$$

By washing with cold water, the aniline hydrochloride is removed, and the residue, treated with potash, yields the diatomic base in a state of purity. It is crystalline, insoluble in water, soluble in alcohol and in ether.

PHENYLENE-DIAMINE, $C_6H_8N_2 = N_2H_4(C_6H_4)''$. — This base is formed by treating dinitrobenzene with acetic acid and iron filings, $C_6H_4(NO_2)_2 + 6H_2 = 4H_2O + C_6H_8N_2$, like aniline from mononitrobenzene. Freshly distilled, phenylene-diamine presents itself as a slightly-colored, heavy oil, which, like phenylamine, has a tendency to assume a brown color on exposure to the air. The base gradually solidifies into a mass of crystals, which become hard and white by washing with ether. The melting point of phenylene-diamine is 63° C. (145° F.), the boiling point near 280° C. (536° F.); it distils without alteration. This substance is very soluble in water and

alcohol, less soluble in ether. It combines with 2 molecules of acid, forming well crystallized, rather soluble salts.

The distillation of dinitrotoluene and dinitrocumene with acetic acid and iron filings produces the corresponding bases, toluylene-diamine, $C_7H_{10}N_2$, and cumylene-diamine, $C_8H_{12}N_2$, which in their properties and chemical deportment bear a great resemblance to phenylene-diamine.

CARBODIPHENYL-TRIAMINE, OR MELANILINE, $C_{13}H_{13}N_3 = N_3\left\{\begin{matrix}(C_6H_5)_2\\ C^{iv}\\ H_3\end{matrix}\right.$.—The action of dry cyanogen chloride upon anhydrous aniline gives rise to the formation of a resinous substance, which is the hydrochloride of melaniline. Dissolved in water and mixed with potash, the above salt yields melaniline in the form of an oil, which rapidly solidifies to a beautiful crystalline mass. The following equation represents its formation: $2C_6H_7N + CNCl = C_{13}H_{14}N_3Cl$.

Melaniline treated with chlorine, bromine, iodine, or nitric acid, yields basic substitution-products, in which invariably two atoms of hydrogen are replaced. It combines with two equivalents of cyanogen, and forms salts with acids, most of which are crystallizable.

CARBOTRIPHENYL-TRIAMINE, OR PHENYL-MELANILINE, $C_{19}H_{17}N_3 = N_3H_2C^{iv}(C_6H_5)_3$. —Aniline, when exposed to the action of carbon tetrachloride at a temperature of 150° C. (302° F.), solidifies into a resinous mass, consisting of a mixture of the hydrochlorides of rosaniline (p. 746), and of several other bases, from which, by appropriate treatment, a beautiful basic compound may be extracted, constituted as above. The formation of this body, which in its properties closely resembles melaniline, may be represented by the equation:

$$6C_6H_7N + CCl_4 = 3(C_6H_7N \cdot HCl) + C_{19}H_{17}N_3 \cdot HCl.$$

Melaniline is sometimes represented as cyano-diphenyl-diamine, $N_2H_3(CN)(C_6H_5)_2$, and phenyl-melaniline as cyano-triphenyl-diamine, $N_2H_2(CN)(C_6H_5)_3$; but these can scarcely be regarded as true formulæ of diamines, inasmuch as they contain only monatomic radicals, and may therefore be resolved into formulæ of monamines.

Aniline Colors.

Aniline has during the last few years found an extensive application in the arts, a long series of coloring matters unequalled in brilliancy and beauty having, by the action of different oxidizing agents, been produced from it. It was Mr. W. H. Perkin who had first the happy idea of applying practically the well-known property possessed by aniline, of forming violet and blue solutions when treated with a solution of chloride of lime or chromic acid. He succeeded in fixing these colors, and bringing them into a form adapted for the dyer. We will here notice some of the most important of these coloring matters.

ANILINE-PURPLE, MAUVE.—According to Mr. Perkin, mauve is prepared by mixing solutions of aniline sulphate and potassium bichromate in equivalent proportions, and allowing the mixture to stand for several hours; the black precipitate formed is filtered off and purified from admixed potassium sulphate by washing with water; it is then dried and freed from resinous matter by repeated digestion with coal-tar naphtha, and finally dissolved in boiling alcohol. For its further purification, the alcoholic solution is evaporated to dryness, the substance is dissolved in a large

quantity of boiling water, reprecipitated with caustic soda, washed with water, and dissolved in alcohol; and the filtered solution is evaporated to dryness. Mauve thus prepared forms a brittle substance, having a beautiful bronze-colored surface: it is difficultly soluble in cold water, although it imparts a deep purple color to that liquid: it is more soluble in hot water, very soluble in alcohol, nearly insoluble in ether and hydrocarbons: it dissolves in concentrated acetic acid, from which it crystallizes. Mauve is the sulphate of a base called *mauveïne*, having the composition $C_{27}H_{24}N_4$, and capable of forming numerous crystalline salts with acids.

Aniline-red, Rosaniline, $C_{20}H_{19}N_3$. — This substance occurs more or less pure in commerce under the names *roseine*, *fuchsine*, *magenta*, *azaleine*, &c. A red color had been observed at different times in experimenting with aniline, more especially when that substance was digested with Dutch liquid. The red coloring matter, though still impure, was first obtained in a separate state from the product formed by digesting aniline with carbon tetrachloride at 150°, in which reaction it is formed, together with carbotriphenyltriamine. It was M. Verguin who first prepared it upon a large scale by the action of stannic chloride upon aniline. Since that time it has been produced by the action of mercuric salts, arsenic acid, and many other oxidizing agents, upon aniline. The most advantageous mode of preparation is the following: A mixture of 12 parts of the dry arsenic acid which occurs in commerce, and 10 parts of aniline, is heated to 120° or 140° C. (250°–280° F.), for about six hours: a little water may be added with advantage. The product, which is a hard mass possessing the lustre of bronze, is dissolved in hot water and precipitated by a slight excess of soda: the precipitate when washed with water, and dissolved in acetic acid, forms the roseine of commerce. In order to purify this still crude substance, it is boiled with an excess of soda, to separate any aniline that it may contain; and the washed precipitate is dissolved in very dilute mineral acid, filtered from undissolved tarry matter, and re-precipitated with alkali. The compounds of rosaniline with one molecule of acid are beautifully crystallized substances, which in the dry state possess a green color with golden lustre; with water they furnish a very intensely colored red solution. The free base, first obtained by Mr. Nicholson, presents itself in colorless crystalline plates, insoluble in water, soluble in alcohol and ether, with a red color, which it also acquires on exposure to the air. Rosaniline in the anhydrous state is represented by the formula $C_{20}H_{19}N_3$, and in the hydrated state, such as it assumes when isolated from its compounds, by the formula $C_{20}H_{19}N_3 . H_2O$. It is a triamine capable of combining with one, two, or three equivalents of acid. The aniline reds of commerce are saline compounds, more or less pure, of rosaniline with one equivalent of acid. The acetate, which is chiefly found in commerce in England, has been prepared by Mr. Nicholson in splendid crystals of very considerable dimensions, having the composition $C_{20}H_{19}N_3 . C_2H_4O_2$. In France, the chloride is chiefly employed; its formula is $C_{20}H_{19}N_3 . HCl$. The action of ammonium sulphide upon rosaniline gives rise to *leucaniline*, $C_{20}H_{21}N_3$, a base containing two additional atoms of hydrogen. This base is itself colorless, and forms colorless salts containing 3 equivalents of acid, such as $C_{20}H_{21}N_3 . HCl$. Oxidizing agents reproduce rosaniline.

The molecular constitution of rosaniline has not been distinctly made out. Neither is its mode of formation thoroughly understood; but one very important fact has been brought to light by the researches of Hofmann, and confirmed by the experience of manufacturers — namely, that pure aniline, from whatever source it may be obtained, is incapable of furnishing aniline-red. Commercial aniline prepared from coal-tar always in fact contains toluidine as well as aniline; and Hofmann has shown that the

presence of this base, together with aniline, is essential to the formation of the red dye. Toluidine by itself is just as incapable of yielding the red as pure aniline, but when a mixture of pure aniline and pure toluidine is treated with stannic or mercuric chloride, or with arsenic acid, the red coloring matter is immediately produced. Its formation may perhaps be represented by the equation:

$$\underset{\text{Aniline.}}{C_6H_7N} + \underset{\text{Toluidine.}}{2C_7H_9N} = \underset{\text{Rosaniline.}}{C_{20}H_{19}N_3} + 3H_2$$

Rosaniline is doubtless a triamine, and the formula $N_3(C_7H_6)''_2.(C_6H_4)''H_3$ has been suggested as the rational expression of its constitution. This, however, is not the formula of a true triamine, since it contains only bivalent radicals, and may be resolved into $NH_3 + N_2(C_7H_6)''_2(C_6H_4)''$, or $N(C_6H_4)''H + N_2(C_7H_6)''_2H_2$.

Aniline-blue and Aniline-violet.—MM. Girard and De Laire obtained aniline-blue by digesting rosaniline with an excess of aniline at 150°–160° C. (300°–320° F.). Together with aniline-blue, which is the principal product of the reaction, several other coloring matters (violet and green) and indifferent substances are formed, considerable quantities of ammonia being invariably evolved. The crude blue is purified by treating it successively with boiling water acidified with hydrochloric acid, and with pure water. The blue coloring matter is said to be obtained from its boiling alcoholic solution in brilliant needles. It consists of the hydrochloride of *triphenyl-rosaniline*, $C_{20}H_{16}(C_6H_5)_3N_3$. By heating rosaniline with ethyl-iodide, Dr. Hofmann * has obtained an aniline-violet, having the composition of hydriodide of *triethyl-rosaniline*, $C_{20}H_{16}(C_2H_5)_3N_3$. Another aniline-violet is produced by heating rosaniline with a quantity of aniline less than sufficient to form aniline-blue.

Aniline-yellow, Chrysaniline.—In the preparation of aniline-red, a considerable quantity of secondary products is produced, from which Mr. Nicholson has succeeded in extracting a yellow coloring matter. This substance, which has been called *chrysaniline*, contains $C_{20}H_{17}N_3$: it is also a well-defined base, forming two series of salts, the majority of them being very well crystallized. The two hydrochlorides of chrysaniline are $C_{20}H_{17}N_3.HCl$, and $C_{20}H_{17}N_3.2HCl$. The nitrate of chrysaniline is so insoluble in water, that nitric acid may be precipitated even from a dilute solution of nitrates by means of the more soluble hydrochlorate or acetate of chrysaniline. Chrysaniline is intimately related to rosaniline and leucaniline, differing from the former by 2 and from the latter by 4 atoms of hydrogen:

Chrysaniline . . .	$C_{20}H_{17}N_3$
Rosaniline . . .	$C_{20}H_{19}N_3$
Leucaniline . . .	$C_{20}H_{21}N_3$.

APPENDIX TO THE ALCOHOLIC AMMONIAS.

Under this head we shall include certain artificial organic bases, the molecular constitution of which has not been very distinctly made out; also the natural bases or alkaloïds found in living organisms; the phosphorus, arsenic, and antimony bases, analogous in composition to the amines; and certain other compounds of organic radicals with metals.

* Proceedings of the Royal Society, xiii. 13.

I. — Artificial Organic Bases obtained from various Sources.

BASES OBTAINED BY DESTRUCTIVE DISTILLATION.

The destructive distillation of organic substances has furnished a rich harvest of basic compounds. A few of the more interesting may here be noticed.

CHINOLINE (LEUCOLINE), C_9H_7N. — Quinine, cinchonine, strychnine, and probably other bodies of this class, when distilled with a very concentrated solution of potash, yield an oily product resembling aniline in many respects, and possessing strong basic powers: it is, however, less volatile than that substance, and boils at 235° C. (455° F.). When pure, it is colorless, and has a faint odor of bitter almonds. Its density is 1·081. It is slightly soluble in water, and miscible in all proportions with alcohol, ether, and essential oils. Chinoline forms salts with acids, which, generally speaking, do not crystallize very freely. Chinoline is a tertiary monamine. When digested with ethyl iodide, it yields iodide of ethylchinoline, $C_{11}H_{12}NI = C_9H_7(C_2H_5)NI$. Treatment of this iodide with silver oxide liberates the base $C_{11}H_{12}N(HO)$, which exhibits all the characters of the ammonium bases, being powerfully alkaline, easily soluble in water, and not volatile. Mr. C. Greville Williams has shown that the basic oil obtained by distilling cinchonine contains, in addition to chinoline, two other bases of very similar properties, to which the names of *lepidine* and *cryptidine* have been given. Lepidine contains $C_{10}H_9N$, cryptidine $C_{11}H_{11}N$.

CHINOLINE-BLUE, CYANINE. — The action of amyl iodide upon chinoline gives rise to iodide of amylchinoline, $C_{14}H_{18}NI$. Addition of an excess of soda to an aqueous solution of this iodide produces a black resinous precipitate, which dissolves in alcohol with a magnificent blue color. This precipitate is the iodide of a new base, discovered by Mr. C. G. Williams, which has been called *cyanine*. The color of this body is unfortunately very fugitive. According to recent researches,* the formation of the new iodide is represented by the following equation: $2C_{14}H_{18}NI = C_{28}H_{35}N_2I + HI$.

PICOLINE, C_6H_7N. — Dr. Anderson has described under this name a volatile, oily base, which is present in certain varieties of coal-tar naphtha, being there associated with aniline, chinoline, and several other volatile substances but imperfectly understood. It is separated without difficulty from the two bases just mentioned, by distillation, in virtue of its superior volatility. Picoline, when pure, is a colorless, transparent, limpid liquid, of powerful and persistent odor, and acrid, bitter taste. It is unaffected by a cold of —18°. It is extremely volatile, evaporates rapidly in the air, and does not become brown like aniline when kept in an ill-stopped bottle. Picoline has a sp. gr. of 0·955, and boils at 133° C. (271° F.). It mixes in all proportions with pure water, but is insoluble in caustic potash and most saline solutions. The alkalinity of this substance is exceedingly well marked: it restores the blue color of reddened litmus, and forms a series of crystallizable salts. It is isomeric with aniline, but completely distinguished from that body by numerous characteristic reactions.

BASES FROM ANIMAL OIL.

The oily liquid obtained by the distillation of bones and animal matter generally, frequently designated by the term Dippel's Oil, contains several

* *Hofmann*, Compt. Rend. lv. 849.

volatile organic bases. Together with some of the substances already described, such as methylamine, ethylamine, picoline, and aniline, Dr. Anderson has found in it several peculiar bases.

Petinine, $C_4H_{11}N$.—The properties of this substance are very analogous to those of biethylamine and triethylamine. It has the same composition as biethylamine, but differs from it by its higher boiling-point, which is 79·5° C. (175° F.), that of biethylamine being 57·5° C. (135° F.) (p. 736). Some chemists are inclined to explain this difference by assuming that petinine is identical with *butylamine*, $NH_2(C_4H_9)$. This assumption may be correct, but is not as yet supported by any experimental evidence. The true butylamine has been obtained by M. Wurtz from butyl-alcohol in the same manner as ethylamine is obtained from common alcohol.

Pyridine, C_5H_5N, much resembles picoline, and is obtained by repeatedly rectifying the bases of Dippel's oil, which distil at 115° C. (239° F.).

Lutidine, C_7H_9N. —Oily base contained in the portion which distils at 154° C. (309° F.).

Collidine, $C_8H_{11}N$. —Oily base very similar to the preceding ones. Boiling point 179° C. (354° F.).

To the same series also belongs an oily base, lately isolated by Mr. C. Greville Williams from the basic products of the distillation of Dorsetshire shale, and described by him under the name of *parvoline*. Parvoline is said to contain $C_9H_{13}N$.

It will be observed that these bases, the constituent radicals of which are not yet clearly made out, are isomeric with the homologues of aniline:

?	.	C_5H_5N	. Pyridine.
Aniline	.	C_6H_7N	. Picoline.
Toluidine	.	C_7H_9N	. Lutidine.
Xylidine	.	$C_8H_{11}N$	. Collidine.
Cumidine	.	$C_9H_{13}N$	. Parvoline.
Cymidine	.	$C_{10}H_{15}N$.	

The first term of the aniline series, and the last of the pyridine series, are unknown. The bases of the aniline series are primary, those of the pyridine series tertiary monamines.

Pyrrol, C_4H_5N. —This substance was first observed by Runge in coal-tar; Anderson afterward obtained it from animal oil. It has the properties of a very weak base, the compounds of which with acids are destroyed by boiling with water. To prepare pyrrol, the bases of animal oil are dissolved in sulphuric acid; the solution, when submitted to protracted ebullition, retains the stronger bases, allowing the pyrrol to pass over. The distillate is heated with solid potassium hydrate, when the pyrrol combines slowly with the alkali, admixed impurities being volatilized. By dissolving the potassium-compound in water, the pyrrol separates as an oily liquid, floating on the surface of the solution. Pyrrol is colorless, insoluble in water and alkalies, slowly soluble in acids: it has an ethereal odor resembling that of chloroform, a specific gravity = 1·077, and boils at 133° C. (271° F.). Pyrrol is easily recognized by the purple color which it imparts to fir-wood moistened with hydrochloric acid.

By heating an acid solution of pyrrol, a red, flaky substance, *pyrrol-red*, is produced, containing $C_{12}H_{14}N_2O_2$, the formation of which is represented by the following equation:

$$3C_4H_5N + H_2O = C_{12}H_{14}N_2O + NH_3.$$

BASES OBTAINED BY THE ACTION OF AMMONIA UPON ALDEHYDES.

The bodies called *hydramides*, produced by the action of ammonia on furfurol (p. 695), and on the aldehydes of the aromatic series, are neutral substances, not capable of uniting with acids; but, when boiled with aqueous potash, they are converted, without addition or abstraction of any elements whatever, into isomeric compounds, which are strong bases, combining readily with acids and forming definite salts.

Furfurine, $C_{15}H_{12}N_2O_3$,* is formed in the manner just described from furfuramide, a hydramide obtained by the action of ammonia on furfurol (p. 695). It is a powerful organic base, forming with acids a series of beautiful crystallizable salts, decomposing at a boiling heat the saline compounds of ammonia. Furfurine is very sparingly soluble in cold water, but dissolves in about 135 parts at about 100°. Alcohol and ether dissolve it freely: the solutions have a strong alkaline reaction. It melts below the boiling point of water, and, when strongly heated, inflames and burns with a red and smoky light, leaving but little charcoal. Its salts are intensely bitter.

Amarine (Benzoline), $C_{21}H_{18}N_2$. — Hydrobenzamide, produced by the action of ammonia on pure bitter-almond oil (p. 690), when long boiled with a solution of caustic potash, suffers the same kind of change as furfuramide, becoming entirely converted into the isomeric base called *amarine*. Precipitated by ammonia from a cold solution of the hydrochloride or sulphate, amarine separates in white curdy masses, which when washed and dried become greatly reduced in volume. In this state it becomes strongly electric by friction with a spatula. It is insoluble in water, but dissolves abundantly in alcohol: the solution is highly alkaline to test-paper, and if sufficiently concentrated, deposits the amarine on standing in small, colorless, prismatic crystals. Below 100° it melts, and on cooling assumes a glassy or resinous condition. Strongly heated in a retort, it decomposes, with production of ammonia, a volatile oil not yet examined, and a new body, *pyrobenzoline* or *lophine*, $C_{21}H_{16}N_2$ (?), which appears to be a feebly basic substance, insoluble in water, soluble in boiling alcohol. It is fusible by moderate heat, and on cooling becomes a mass of colorless radiating needles or plates. The salts of amarine are mostly sparingly soluble; the sulphate, nitrate, and hydrochloride are crystallizable and very definite.

Thialdine, $C_6H_{13}NS_2$. — This base is obtained by dissolving the crystalline compound of aldehyde with ammonia (p. 687) in from 12 to 16 parts of water, mixing the solution with a few drops of caustic ammonia, and then subjecting the whole to a feeble stream of sulphuretted hydrogen. After a time the liquid becomes turbid, and deposits thialdine as a white crystalline substance. It is separated, washed, dissolved in ether, and the solution mixed with alcohol and left to evaporate spontaneously, by which means the base is obtained in large, regular, rhombic crystals, having the form of gypsum. The crystals are heavier than water, transparent and colorless. They refract light strongly. Thialdine has a somewhat aromatic odor, melts at 43·3°, and volatilizes slowly at common temperatures. It distils unchanged with the vapor of water, but decomposes when heated alone. It is very sparingly soluble in water, easily in alcohol and ether. It has no action on vegetable colors, but dissolves freely in acids, forming crystallizable salts. Heated with slaked lime, it is said to yield chinoline.

A very similar compound containing selenium has been prepared.

* This remarkable substance, the nearest approach to the native alkaloïds yet made, was discovered by the author of this manual. — Eds.

Alaline, $C_3H_7NO_2$, produced by treating acetic aldehyde with hydrocyanic and hydrochloric acids, and *leucine*, $C_6H_{13}NO_2$, obtained, in like manner, from valeric aldehyde, are likewise bases, forming definite salts with acids; but they are also acids, capable of forming salts by exchanging their hydrogen for metals; they have indeed the composition of amidopropionic and amidocaproic acids, and as such have been already described (pp. 615, 619). *Glycocine*, $C_2H_5NO_2$ (p. 614), is another body of the same series, and possessing similar properties.

II. — Natural Organic Bases, or Alkaloïds.

The organic alkaloïds constitute a remarkable and most interesting group of bodies: they are met with in various plants, some of them also in the animal organism. They are, for the most part, sparingly soluble in water, but dissolve in hot alcohol, from which they often crystallize in a very beautiful manner on cooling. Several of them, however, are oily, volatile liquids. The taste of the vegeto-alkalies, when in solution, is usually intensely bitter, and their action upon the animal economy exceedingly energetic. They all contain a considerable quantity of nitrogen, and are very complicated in constitution, having high combining numbers. This class of bodies is very numerous; but the limits of this elementary work permit us to study only the more important members included in it.

None of the organic bases occurring in plants have yet been formed by artificial means; and their constitution is far from being completely understood. There can be no doubt, however, that the natural alkaloïds, like the artificial bases, are substitution-products of ammonia. Many of them, when submitted to the action of methyl or ethyl iodide, are capable of absorbing a smaller or greater number of equivalents of methyl and ethyl, and their deportment with these alcohol-iodides permits us to ascertain with great precision their degree of substitution. If a natural alkaloïd, when submitted to the action of ethyl iodide, be found to require for conversion into a base of the formula,

$$N\left\{\begin{matrix}A\\B\\C\\D\end{matrix}\right\}OH,$$

either 1, or 2, or 3 equivalents of ethyl, we may infer that the alkaloïd in question belongs to the class of bases represented by the formulæ:

$$N\left\{\begin{matrix}A\\B\\C\end{matrix}\right. \quad \text{or} \quad N\left\{\begin{matrix}A\\B\\H\end{matrix}\right. \quad \text{or} \quad N\left\{\begin{matrix}A\\H\\H\end{matrix}\right.$$

i. e., that it is a tertiary, a secondary, or a primary monamine. All natural alkaloïds which have been examined, with the exception of conine, are tertiary bases.

Morphine, or **Morphia**, $C_{17}H_{19}NO_3$. — This is the chief active principle of opium: it is the most characteristic body of the group, and the earliest known, dating back to the year 1804, when it was discovered by Sertürner.

Opium, the inspissated juice of the poppy-capsule, is a very complicated substance, containing, besides morphine, a host of other alkaloïds in very variable quantities, combined with sulphuric acid and meconic acid (p. 679). In addition to these, there are gummy, resinous, and coloring matters, caoutchouc, &c., besides mechanical impurities, as chopped leaves. The

opium of Turkey is the most valuable, and contains the largest quantity of morphine: the opiums of Egypt and of India are considerably inferior. Opium has been produced in England of the finest quality, but at great cost.

If ammonia be added to a clear, aqueous infusion of opium, a very abundant buff-colored or brownish-white precipitate falls, which consists principally of morphine and narcotine, rendered insoluble by the withdrawal of the acid. The product is too impure, however, for use. The chief difficulty in the preparation of these substances is to get rid of the coloring matter, which adheres with great obstinacy, redissolving with the precipitates, and being again in part thrown down when the solutions are saturated with an alkali. The following method, which succeeds well upon a small scale, will serve to give the student some idea of a process very commonly pursued when it is desired to isolate at once an insoluble organic base, and the acid with which it is in combination: A filtered solution of opium in tepid water is mixed with lead acetate in excess; the precipitated lead meconate is separated by a filter, and through the solution containing morphine acetate, now freed to a considerable extent from color, a stream of sulphuretted hydrogen is passed. The filtered and nearly colorless liquid, from which the lead has been thus removed, may be warmed to expel the excess of gas, once more filtered, and then mixed with a slight excess of caustic ammonia, which throws down the morphine and narcotine: these may be separated by boiling ether, in which the latter is soluble. The lead meconate, well washed, suspended in water, and decomposed by sulphuretted hydrogen, yields a solution of meconic acid.

Morphine and its salts are advantageously prepared, on the large scale, by the process of Dr. Gregory. A strong infusion of opium is mixed with a solution of calcium chloride, free from iron; calcium meconate, which is nearly insoluble, then separates, while the hydrochloric acid is transferred to the alkaloïds. By duly concentrating the filtered solution, the hydrochloride of morphine may be made to crystallize, while the narcotine and other bodies are left behind. Repeated recrystallization, and the use of animal charcoal, then suffice to whiten and purify the salt, from which the base may be precipitated in the pure state by ammonia. Other processes have been proposed, as that of M. Thiboumery, which consists in adding slaked lime in excess to an infusion of opium, by which the meconic acid is rendered insoluble, while the morphine is taken up with ease by the alkaline earth. By *exactly* neutralizing the filtered solution with hydrochloric acid, the morphine is precipitated, but in a somewhat colored state.

Morphine, when crystallized from alcohol, forms small but very brilliant prismatic crystals, which are transparent and colorless. It requires at least 1000 parts of water for solution, tastes slightly bitter, and has an alkaline reaction. These effects are much more evident in the alcoholic solution. It dissolves in about 30 parts of boiling alcohol, and with great facility in dilute acids; it is also dissolved by excess of caustic potash or soda, but scarcely by excess of ammonia. When heated in the air, morphine melts, inflames like a resin, and leaves a small quantity of charcoal, which easily burns away.

Morphine in powder strikes a deep-bluish color with neutral ferric salts, decomposes iodic acid with liberation of iodine, and forms a deep-yellow or red compound with nitric acid: these reactions are by some considered characteristic.

Crystallized morphine contains $C_{17}H_{19}NO_3 . H_2O$.

The most characteristic and best-defined salt of this base is the *hydrochloride*. It crystallizes in slender, colorless needles, arranged in tufts or stellated groups, soluble in about 20 parts of cold water, and in its own weight at the boiling heat. The crystals contain 3 molecules of water. The *sulphate*, *nitrate*, and *phosphate* are crystallizable salts: the *acetate* crys-

tallizes with great difficulty, and is usually sold in the state of a dry powder. The artificial *meconate* is sometimes prepared for medicinal use.

An alcoholic solution of morphine, heated in sealed tubes with methyl iodide, forms a crystalline compound, $C_{18}H_{22}NO_3I = C_{17}(H_{19}CH_3)NO_3I$; this substance yields, with silver oxide, a very alkaline solution, obviously containing an ammonium base. Morphine is therefore a tertiary amine, the group $C_{17}H_{19}O_3$ representing one or several radicals, which are together capable of replacing 3 atoms of hydrogen.

Narcotine. — The *marc*, or insoluble portion of opium, contains much narcotine, which may be extracted by boiling with dilute acetic acid. From the filtered solution the narcotine is precipitated by ammonia, and afterwards purified by solution in boiling alcohol, and filtration through animal charcoal. Narcotine crystallizes in small, colorless, brilliant prisms, which are nearly insoluble in water. The basic powers of narcotine are very feeble: it is destitute of alkaline reaction, and although freely soluble in acids, refuses, for the most part, to form with them crystallizable compounds.

According to Matthiessen and Foster, narcotine contains $C_{22}H_{23}NO_7$.

Narcotine yields some curious products by the action of oxidizing agents, as a mixture of dilute sulphuric acid and manganese dioxide, or a hot solution of platinic chloride. They have been chiefly studied by Wöhler, Blyth, Anderson, and lately also by Matthiessen and Foster. The most important of these is *opianic* acid, a substance forming colorless, prismatic, reticulated crystals, sparingly soluble in cold, easily in hot water. It melts when heated, but does not sublime. After fusion it becomes quite insoluble in dilute alkalies, but without change of composition. This acid forms crystallizable salts and an ether: it contains $C_{10}H_{10}O_5$. The ammonia-salt, by evaporation to dryness, yields a nearly white insoluble powder, called *opiammone*, containing $C_{20}H_{19}NO_8$, convertible by strong acids into opianic acid and ammonia. Sulphurous acid yields with opianic acid two products containing sulphur. A basic substance, *cotarnine*, $C_{12}H_{13}NO_3$, is contained in the mother-liquor from which opianic acid has crystallized: it forms a yellow crystalline mass, very soluble, of bitter taste, and feebly alkaline reaction. Its hydrochloride is a well-defined salt. The transformation of narcotine into opianic acid and cotarnine is represented by the equation:

$$C_{22}H_{23}NO_7 + O = C_{10}H_{10}O_5 + C_{12}H_{13}NO_3.$$

Another basic substance, *narcogenine*, was accidentally produced in an attempt to prepare cotarnine with platinic chloride. It formed long orange-colored needles, and contained $C_{18}H_{19}NO_5$.

By heating opianic acid with a strong solution of potash, it is converted into a crystallizable neutral and volatile substance called *meconin*, $C_{10}H_{10}O_4$, and a bibasic crystallizable acid, termed *hemipinic acid*, $C_{10}H_{10}O_6$:

$$2C_{10}H_{10}O_5 = C_{10}H_{10}O_4 + C_{10}H_{10}O_6.$$

Hemipinic acid, treated with hydriodic acid, splits up into methyl iodide, carbonic acid, and hypogallic, $C_7H_6O_4$, the relation of which to gallic acid has already been mentioned (p. 667). When cotarnine is gently heated with very dilute nitric acid, it is converted into methylamine nitrate and *cotarnic acid*, a bibasic acid containing $C_{11}H_{12}O_5$:

$$C_{12}H_{13}NO_3 + 2H_2O + NO_3H = CH_6N.NO_3 + C_{11}H_{12}O_5.$$

Codeine, $C_{18}H_{21}NO_3$. — Hydrochloride of morphine, prepared directly from opium, as in Gregory's process, contains codeine-salt. On dissolving it in water, and adding a slight excess of ammonia, the morphine is precipitated, and the codeine left in solution. Pure codeine crystallizes, by

spontaneous evaporation, in colorless transparent octohedrons: it is soluble in 80 parts of cold, and 17 of boiling water, has a strong alkaline reaction, and forms crystallizable salts.

With ethyl iodide codeine forms a crystalline iodide, $C_{20}H_{26}NO_3I = C_{18}H_{21}(C_2H_5)NO_3I$, furnishing with silver oxide a soluble base. Codeine being considered as a tertiary monamine, the group $C_{18}H_{21}O_3$ represents 3 atoms of hydrogen.

Codeine is homologous with morphine, $C_{18}H_{21}NO_3$. It has been the subject of a careful investigation by Dr. Anderson, who has prepared a great number of its derivatives, all of which establish the formula above given.

Thebaine or **Paramorphine.** — This substance is contained in the precipitate formed by calcium hydrate in a strong infusion of opium, in Thiboumery's process for preparing morphine. The precipitate is well washed, dissolved in dilute acid, and mixed with ammonia in excess, and the thebaine is thrown down crystallized from alcohol. When pure, it forms colorless needles like those of narcotine, but sparingly soluble in water, readily soluble in the cold in alcohol and ether. It melts when heated, and decomposes at a high temperature. With dilute acids it forms crystallizable compounds, and when isolated and in solution has a powerfully alkaline reaction.

A series of other bases, *papaverine*, $C_{20}H_{21}NO_4$, *pseudo-morphine*, *narceine*, $C_{23}H_{29}NO_9$, *opianine*, and *porphyroxine*, are also — at least occasionally — contained in opium: they are of small importance, and comparatively little is known respecting them. A considerable number of derivatives of papaverine have been prepared, which confirm the formula above given for it.

Cinchonine and **Quinine.** — It is to these vegeto-alkalies that the valuable medicinal properties of the Peruvian barks are due. They are associated in the barks with sulphuric acid, and with a special acid, called the *quinic* or *kinic*. Cinchonine is contained in largest quantity in the pale bark, or *Cinchona condaminea;* quinine in the yellow bark, or *Cinchona cordifolia;* the *Cinchona oblongifolia* contains both.

The simplest, but not the most economical, method of preparing these substances is to add a slight excess of calcium hydrate to a strong decoction of the ground bark in acidulated water, wash the precipitate which ensues, and boil it in alcohol. The solution, filtered while hot, deposits the vegeto-alkali on cooling. When both bases are present, they may be separated by converting them into sulphates: the quinine-salt is the less soluble of the two, and crystallizes first.

Pure cinchonine, or cinchonia, crystallizes in small, but beautifully brilliant, transparent, four-sided prisms. It is but very feebly soluble in water, dissolves readily in boiling alcohol, and has but little taste, although its salts are excessively bitter. It is a powerful base, neutralizing acids completely, and forming a series of crystallizable salts. Cinchonine turns the plane of polarization to the right.

Quinine or quina, much resembles cinchonine: it does not crystallize so well, however, and is much more soluble in water: its taste is intensely bitter. Quinine turns the plane of polarization toward the left.

Cinchonine is composed of . . . $C_{20}H_{24}N_2O$, and
Quinine of . . . . . $C_{20}H_{24}N_2O_2$.

Quinine sulphate is manufactured on a very large scale for medicinal use: it crystallizes in small white needles, which give a neutral solution. This substance contains $2C_{20}H_{24}N_2O_2 . SO_4H_2 . 7$ Aq. Its solubility is much increased by the addition of a little sulphuric acid, whereby the acid salt, $C_{20}H_{24}N_2O_2 . SO_4H_2 . 7$ Aq., is formed. A very interesting compound has been produced by Dr. Herapath, by the action of iodine upon quinine sul-

phate. It is a crystalline substance of a brilliant emerald color, which appears to consist of equal equivalents of the sulphate of quinine and of iodine. This remarkable compound possesses the optical properties of the tourmaline (p. 92).

Cinchonine and quinine yield with methyl iodide, compounds represented respectively by the formulæ $C_{20}H_{24}(CH_3)N_2OI$ and $C_{20}H_{24}(CH_3)N_2O_2I$, which are converted by silver oxide into soluble bases analogous to tetrethyl-ammonium hydrate.

Quinidine.—In manufacturing quinine sulphate, a new base has been obtained, which differs from quinine in some of its physical properties, but is said to have the same composition. It has been described under the name of *quinidine*, and appears to have the same medicinal properties as quinine. The substance has been carefully examined by Pasteur, whose researches have led to the following interesting results:

The substance which is found in commerce under the name of quinidine is generally a mixture of two alkaloïds, of which the one is isomeric with quinine, and the other with cinchonine. Pasteur designates these two substances respectively as *quinidine* and *cinchonidine*. They differ from quinine and cinchonine in several properties, but particularly in their deportment with polarized light: for while quinine turns the plane of polarization considerably towards the *left*, quinidine exerts a powerful action towards the *right*. Again, while cinchonine deflects considerably towards the *right*, the action of the isomeric cinchonidine is in the opposite direction — namely, towards the *left*. It is evident that quinine and quinidine on the one hand, and cinchonidine and cinchonine on the other, stand to each other in about the same relation as levo- and dextro-tartaric acids (p. 677). Nor are the terms wanting which correspond to racemic acid. Pasteur has, in fact, proved that both quinine and quinidine, and likewise cinchonine and cinchonidine, are peculiarly modified by the action of heat: exposed for several hours to a temperature varying between 120° and 130° C. (248°–256° F.), quinine and quinidine are converted into a third isomeric alkaloid, which Pasteur terms *quinicine*, while cinchonine and cinchonidine furnish an isomeric *cinchonicine* under the same circumstances. In racemic acid the right-handed action of dextro-tartaric, and the left-handed action of levo-tartaric acid, are exactly balanced, racemic acid possessing no longer any action upon polarized light: in quinicine and cinchonicine, such a perfect balance is not observed; both still exert a feeble right-handed action, which is, however, very slight when compared with the rotatory powers of the alkaloïds which give rise to them. The following table exhibits the relations of the six alkaloïds, and their analogy with the racemic group, in a more conspicuous manner:

Quinine *Left-handed, powerfully.*	Quinicine *Right-handed, feebly.*	Quinidine *Right-handed, very powerfully.*
Cinchonine *Right-hunded, very powerfully.*	Cinchonicine *Right-handed, feebly.*	Cinchonidine *Left-handed, powerfully.*
Dextro-tartaric acid *Right-handed.*	Racemic acid *neutral.*	Levo-tartaric acid. *Left-handed.*

Chinoïdine, *Quinoïdine*, or *Amorphous quinine*, is contained in the refuse, or mother-liquors, of the quinine manufacture. In its purest state it forms a yellow or brown resin like mass, insoluble in water, freely soluble in alcohol and ether. It is easily soluble also in dilute acids, and is thence precipitated by ammonia. Quinoïdine possesses powerful febrifuge properties, and is identical in composition with quinine. It evidently bears to quinine

the same relation that uncrystallizable syrup bears to ordinary sugar, being produced from quinine by the heat employed in the preparation.

From *Cusco-* or *Arica-bark*, and likewise from the *Cinchona ovata*, or *white quinquina* of Condamine, a substance denominated *Aricine* or *Cinchovatine* has been extracted: it closely resembles cinchonine, and is said to contain $C_{20}H_{26}N_2O_4$. This formula exhibits a close analogy with the formulæ of cinchonine and quinine. Aricine is useless in medicine.

Strychnine and **Brucine**, also called *Strychnia* and *Brucia*, are contained, together with several still imperfectly known bases, in *Nux vomica*, in *St. Ignatius' bean*, and in *false Angustura bark*. Strychnine and brucine are generally associated with a peculiar acid, called *igasuric acid*. Nux vomica seeds are boiled in dilute sulphuric acid until they become soft: they are then crushed, and the expressed liquid is mixed with excess of calcium hydrate, which throws down the alkaloïds. The precipitate is boiled in spirits of wine of sp. gr. 0·850, and filtered hot. Strychnine and brucine are then deposited together in a colored and impure state, and may be separated by cold alcohol, in which the latter dissolves readily.

Pure strychnine crystallizes under favorable circumstances in small but exceedingly brilliant octohedral crystals, which are transparent and colorless. It has a very bitter, somewhat metallic taste (1 part in 1,000,000 parts of water is still perceptible), is slightly soluble in water, and fearfully poisonous. It dissolves in hot, and somewhat dilute spirit, but not in absolute alcohol, ether, or solution of caustic alkali. This alkaloïd may be readily identified by moistening a crystal with concentrated sulphuric acid, and adding to the liquid a crystal of potassium bichromate, when a deep violet tint is produced, which disappears after some time. Strychnine forms with acids a series of well-defined salts, which were examined by Messrs. Nicholson and Abel, who established for strychnine the formula $C_{21}H_{22}N_2O_2$.

Strychnine forms with ethyl iodide a crystalline compound, $C_{21}H_{22}(C_2H_5)N_2O_4I$, converted by silver oxide into a soluble base.

Brucine, $C_{23}H_{26}N_2O_4$, is easily distinguished from the preceding substance, which it much resembles in many respects, by its ready solubility in alcohol, both hydrated and absolute. It dissolves also in about 500 parts of hot water. The salts of brucine are, for the most part, crystallizable.

Veratrine, or **Veratria**, $C_{32}H_{52}N_2O_8$, is obtained from the seeds of *Veratrum sabadilla*. In the pure state it is a white or yellowish-white powder, which has a sharp burning taste, and is very poisonous. It is remarkable for occasioning violent sneezing. It is insoluble in water, but dissolves in hot alcohol, in ether, and in acids: the solution has an alkaline reaction.

A substance called *colchicine*, extracted from the *Colchicum autumnale*, and formerly confounded with veratrine, is now considered distinct: its history is still imperfect.

Harmaline, $C_{13}H_{14}N_2O$. — This compound is extracted by dilute acetic acid from the seeds of the *Peganum harmala*, a plant which grows abundantly on the Steppes of Southern Russia, and the seeds of which are used in dyeing. When pure, it forms yellowish prismatic crystals, soluble in alcohol and dilute acids, but scarcely forming crystallizable salts. By oxidation it gives rise to another compound, *harmine*, $C_{13}H_{12}N_2O$, which also possesses basic properties.

Caffeine, or **Theine**, $C_8H_{10}N_4O_2$. — This remarkable substance occurs in four articles of domestic life, infusions of which are used as beverages over the greater part of the known world—namely, in tea and coffee, in the leaves of *Guarana officinalis*, or *Paullinia sorbilis*, and in those of *Ilex Paraguayensis;*

it will probably be found in other plants. A decoction of common tea, or of raw coffee-berries, previously crushed, is mixed with excess of solution of basic lead acetate. The solution, filtered from the copious yellow or greenish precipitate, is treated with sulphuretted hydrogen to remove the lead, then filtered, evaporated to a small bulk, and neutralized by ammonia. The caffeine crystallizes out on cooling, and is easily purified by animal charcoal. It forms tufts of delicate, white, silky needles, which have a bitter taste, melt when heated with loss of water, and sublime without decomposition. It is soluble in about 100 parts of cold water, and much more easily at the boiling heat, or if an acid be present. Alcohol also dissolves it, but not easily. The basic properties of caffeine are feeble. The salts which it forms with hydrochloric and sulphuric acids are obtained only with difficulty. It forms, however, splendid double salts with platinum tetrachloride and gold trichloride. The products of oxidation of caffeine, which have been studied by Rochleder, are of considerable interest, inasmuch as both their composition and their properties establish a close connection between these products and the derivatives of uric acid. Under the influence of chlorine, caffeine yields *amalic acid*, a substance of feebly acid properties, having the composition of hydrated tetramethyl-alloxantin, $C_8(CH_3)_4N_4O_7 . Aq$. When treated with oxidizing agents, it yields *cholestrophane*, $C_5H_6N_2O_3$, corresponding to parabanic acid of the uric acid series. Cholestrophane may be viewed as dimethyl-parabanic acid; it has, in fact, been obtained by digesting silver parabanate with methyl iodide:

$$C_3Ag_2N_2O_3 + 2CH_3I = 2AgI + C_5H_6N_2O_3.$$

Lastly, the murexide of the caffeine series is formed by the treatment of amalic acid with ammonia, exactly as the true murexide from uric acid is formed by the action of ammonia upon alloxantin. The new murexide imitates its prototype, not only in composition, but likewise in the green metallic lustre of its crystals, and the deep crimson color of its solutions.

Theobromine. — The seeds of the *Theobroma Cacao*, or cacao-nuts, from which chocolate is prepared, contain a crystallizable principle, to which this name is given. It is extracted in the same manner as caffeine, and forms a white, crystalline powder, which is much less soluble than the last-named substance. It contains, according to Glasson, $C_7H_8N_4O_2$. Theobromine is easily soluble in aqueous ammonia; by adding silver nitrate to this solution, and boiling, a crystalline precipitate of silver-theobromine, $C_7H_7AgN_4O_2$, is obtained. By treating this silver compound with methyl iodide, Strecker obtained silver iodide and caffeine: $C_7H_7AgN_4O_2 + CH_3I = AgI + C_8H_{10}N_4O_2$, which may be extracted with alcohol. Caffeine must therefore be regarded as methyl-theobromine. The products obtained from theobromine by oxidation appear to be homologous with several terms of the uric acid series.

Xanthine, $C_5H_4N_4O_2$. — Xanthine was first described by Dr. Marcet under the name of xanthic oxide, which he discovered as a constituent of urinary calculi; recently it has been found among the products of the decomposition of guanine. It is present in nearly every part of the animal organism, and, although in very minute quantities, in urine.

Xanthine, according to Strecker, may be prepared with the greatest facility from guanine (p. 758). Potassium nitrite is added to a solution of guanine in concentrated nitric acid until a powerful evolution of red fumes takes place: the solution is then mixed with a large quantity of water, whereby a yellow substance is precipitated, which, after washing with water, is dissolved in ammonia. A solution of ferrous sulphate is now added

until a black precipitate of iron oxide begins to appear.* The still powerfully ammoniacal solution is filtered and evaporated to dryness; and the residue is extracted with water in order to separate the ammonium sulphate; then dissolved in ammonia, and evaporated. Xanthine is a white, amorphous powder, difficultly soluble in water, soluble in acids, with which it forms crystalline compounds. The sulphate has the composition $2C_5H_4N_4O_2 . SO_4H_2$. Xanthine dissolves with facility in ammonia and potash. Its characteristic property is to dissolve without evolution of gas in nitric acid, and to give on evaporation a deep-yellow residue, which, on addition of ammonia or solution of potash, assumes a yellow-red color. By treatment of silver-xanthine, $C_5H_2Ag_2N_4H_2$, with methyl iodide, Strecker obtained a body isomeric with theobromine, differing, however, in its properties from that substance:

$$C_5H_2Ag_2N_4O_2 + 2CH_3I = 2AgI + C_7H_8N_4O_2.$$

Sarcine (Hypoxanthine), $C_5H_4N_4O$. — This base is a constituent of the flesh of vertebrata. It is best prepared from the mother-liquor of creatin (p. 902), by diluting with water and boiling with cupric acetate, whereby the sarcine is precipitated in combination with cupric oxide. This precipitate is dissolved in nitric acid and mixed with silver nitrate; the crystals, a compound of sarcine nitrate with silver nitrate, are purified by re-crystallization from nitric acid, and are then, by ebullition with an ammoniacal solution of silver nitrate, converted into the compound of sarcine with silver oxide, $C_5H_4N_4O . Ag_2O$, which is decomposed by sulphuretted hydrogen.

Sarcine forms delicate white microscopic needles, difficultly soluble in cold water, easily soluble in boiling water, in dilute acids, ammonia, potash, and baryta-water. Sarcine forms crystallizable salts, containing 1 equivalent of acid. It unites with bases, like guanine, forming crystalline compounds containing 2 equivalents of metallic oxide.

Guanine, $C_5H_5N_5O$. — This base was first obtained from guano; it has also been proved to exist in the pancreatic juice of mammalia, and in the excrement of the spider. To prepare it, guano is boiled with water and calcium hydrate until a portion of the liquid, when filtered, appears but slightly colored: the whole is then filtered, and the filtrate saturated with acetic acid, whereby the guanine is precipitated, mixed with uric acid. It is purified by solution in hydrochloric acid and precipitation by ammonia.

Guanine is a colorless, crystalline powder, insoluble in water, alcohol, ether, and ammonia, soluble in acids and solution of potash. With acids it forms crystallizable salts containing 1 and 2 equivalents of acid: it combines with bases to crystalline compounds containing 2 equivalents of metallic oxide.

Guanine, sarcine, and xanthine bear a great resemblance to each other, and are all found in the animal organism. Guanine, on account of its insolubility in water and ammonia, may easily be separated from the two other substances. To separate xanthine and sarcine, they are converted into the hydrochlorides, which are treated with warm water: xanthine hydrochloride is so little soluble in that liquid, that it may easily be separated from the admixed sarcine hydrochloride.

Guanidine, CH_5N_3. — This substance is prepared from guanine. Guanine is treated with hydrochloric acid and potassium chlorate, whereby it is converted into a mixture of guanidine and parabanic acid. As soon as the guanine is completely dissolved, the liquid is evaporated till the parabanic

* The treatment of guanine with nitric acid gives rise to xanthine and nitroxanthine, which by the action of reducing agents is converted into xanthine. Strecker recommends a ferrous salt for this purpose.

acid has crystallized out. The mother-liquor is treated with a mixture of alcohol and ether, which, separated from the residue and evaporated, yields on evaporation the crude guanidine hydrochloride. The hydrochloride may, by digestion with silver sulphate, be converted into the sulphate, and the latter finally into the free base by addition of baryta-water.

Guanidine thus prepared forms colorless crystals, readily soluble in water and alcohol; the solution has a powerfully alkaline reaction. It absorbs carbonic acid from the air, forming a carbonate $2CH_5N_3 . H_2CO_3$, which has an alkaline reaction, and crystallizes in square prisms. The transformation of guanine into parabanic acid and guanidine is represented by the following equation:

$$C_5H_5N_5O + O_3 + H_2O = C_3H_2N_2O_3 + CH_5N_3 + CO_2.$$

Triethylguanidine. — The action of sodium alcohol upon ethyl cyanate or cyanurate gives rise to a base having the composition $C_7H_{17}N_3$, which is that of triethylguanidine (carbotriethyltriamine). It is formed according to the following equation:

$$3CN(C_2H_5)O + 2C_2H_5NaO = C_7H_{17}N_3 + 2C_2H_4 + CO_2 + Na_2CO_3.$$

Creatin, $C_4H_9N_3O_2 . 2$ Aq. — Creatin was first observed by Chevreul, and has been studied very carefully by Liebig, who obtained it from the soup of boiled meat. It is prepared from the juice of raw flesh by the following process: A large quantity of lean flesh is cut up into shreds, exhausted by successive portions of cold water, strained and pressed. The liquid, which has an acid reaction, is heated to coagulate albumin and coloring matter of blood, and passed through a cloth. It is then mixed with pure baryta-water as long as a precipitate appears, filtered from the deposit of phosphates, and evaporated in a water-bath to a syrupy state. After standing some days in a warm situation, the creatin is gradually deposited in crystals, which are easily purified by re-solution in water and digestion with a little animal charcoal. *

When pure, creatin forms colorless, brilliant, prismatic crystals, which become dull by loss of water at 100°. They dissolve readily in boiling water, sparingly in cold water, and are but little soluble in alcohol. The aqueous solution has a weak bitter taste, followed by a somewhat acrid sensation. In an impure state the solution readily putrefies. Creatin is a neutral body, not combining either with acids or with alkalies. In the crystallized state it contains $C_4H_9N_3O_2 . 2H_2O$.

Creatinine, $C_4H_7N_3O$. — By the action of strong acids, creatin is converted into *creatinine*, a powerful organic base, with separation of the elements of water. The new substance forms colorless prismatic crystals, and is much more soluble in water than creatin: it has a strong alkaline reaction, and forms crystallizable salts with acids.

Creatinine pre-exists to a small extent in the juice of flesh, together with lactic acid and other bodies not yet perfectly examined. It is also found in conjunction with creatin in urine.

Sarcosine, $C_3H_7NO_2$, formed by boiling creatin with baryta-water, has the composition of methyl-glycocine or methyl-amidacetic acid, $C_2H_4(CH_3)NO_2$, and has been already described among the derivatives of acetic acid (p. 614).

* The mother-liquid from flesh from which the creatin has been deposited contains, among other things, a new acid, the *inosinic*, the aqueous solution of which refuses to crystallize. It has a strong acid reaction, and is precipitated in a white amorphous condition by alcohol. It probably contains $C_{10}H_{14}N_2O_{11}$.

Berberine, $C_{21}H_{19}NO_5$, is a substance crystallizing in fine yellow needles, slightly soluble in water, extracted from the root of the *Berberis vulgaris*. It has feeble basic properties. This must not be confounded with *bebeerine*, an uncrystallizable basic substance, from the bark of the *green-heart* tree of Guiana, which has the composition $C_{19}H_{21}NO_3$.

Piperine, $C_{34}H_{38}N_2O_6$. — A colorless, or slightly yellow crystallizable principle, extracted from pepper by the aid of alcohol. It is insoluble in water. Piperine readily dissolves in acids; definite compounds are, however, difficult to obtain.

Conine (*Conicine*, or *Conia*), **Nicotine**, and **Sparteine** differ from the other vegetable bases in physical characters: they are volatile oily liquids. The first is extracted from hemlock, the second from tobacco, and the third from broom (*Spartium Scoparium*). They agree in most of their characters, having high boiling points, very poisonous properties, strong alkaline reaction, and the power of forming crystallizable salts with acids. The formula of nicotine is $C_{10}H_{14}N_2$; that of conine, $C_8H_{15}N$; and that of sparteine, $C_{10}H_{26}N_2$.

Closely allied to conine is *conhydrine*, $C_8H_{17}NO$, a crystalline base, extracted by Wertheim from hemlock. When distilled with anhydrous phosphoric acid, it splits into conine and one molecule of water.

A mixture of nicotine with methyl or ethyl iodide solidifies after a short time to crystalline masses, containing $C_{10}H_{14}(CH_3)_2N_2I_2$, and $C_{10}H_{14}(C_2H_5)_2N_2I_2$, convertible by silver oxide into soluble bases.

Conine is a secondary monamine. Treated with ethyl iodide, it yields successively two iodine-compounds — namely, $C_8H_{15}(C_2H_5)NI$ and $C_8H_{14}(C_2H_5)_2NI$. The latter is converted by silver oxide into a soluble base.

There are very many other bodies, more or less perfectly known, having to a certain extent the properties of alkaloïds: the following statement of the names and mode of occurrence of a few of them must suffice.

Hyoscyamine (*Daturine*). — A white, crystallizable substance, from *Hyoscyamus niger;* it occurs likewise in *Datura Stramonium*.

Atropine. — Colorless needles, from *Atropa Belladonna;* formula $C_{17}H_{23}NO_3$.

Solanine. — A pearly, crystalline substance, from various solanaceous plants; formula $C_{43}H_{71}NO_{16}$ (?) (p. 582).

Aconitine. — A glassy, transparent mass, from *Aconitum Napellus;* formula $C_{30}H_{47}NO_7$.

Delphinine. — A yellowish, fusible substance, from the seeds of *Delphinium Staphisagria*.

Emetine. — A white and nearly tasteless powder from ipecacuanha root.

Curarine. — The arrow-poison of Central America.

III. — Phosphorus, Antimony, and Arsenic Bases.

Phosphorus, antimony, and arsenic being, like nitrogen, either trivalent or quinquivalent, are capable of forming compounds analogous to the amines and the compound ammonium salts. A few of these remarkable compounds will be briefly described in the following paragraphs.

PHOSPHINES.

Paul Thénard, by passing the vapor of methyl chloride over calcium phosphide heated to about 180° C. (356° F.), obtained a mixture of phos-

phoretted bodies, from which he separated three compounds believed to correspond in composition with the three hydrides of phosphorus (p. 215), viz., $P_2(CH_3)$, $P(CH_3)_2$, and $P(CH_3)_3$; these bodies were, however, but very imperfectly investigated. More recently Cahours and Hofmann, by subjecting zinc-methyl and zinc-ethyl to the action of phosphorus trichloride, have obtained saline compounds, from which, by distillation with potash, the bases $P(CH_3)_3$ and $P(C_2H_5)_3$, analogous to the tertiary monamines, may be liberated; thus:

$$\underset{\text{Zinc-ethyl.}}{3Zn(C_2H_5)_2} + 2PCl_3 = 3ZnCl_2 + \underset{\text{Triethyl-phosphine.}}{2P(C_2H_5)_3}.$$

Thriethylphosphine, $C_6H_{15}P = P(C_2H_5)_3$. — This substance is a colorless oil having a very penetrating phosphorus odor, and boiling at 133°. It is slowly oxidized in atmospheric air. The vapor, heated with air or oxygen, explodes. In chlorine gas it burns with separation of carbon, hydrochloric acid and phosphorus pentachloride being produced. With acids it forms crystalline compounds, which are very deliquescent. With iodide of methyl, ethyl, and amyl, it solidifies after a few moments to crystalline compounds, containing respectively $P(C_2H_5)_3(CH_3)I$, $P(C_2H_5)_4I$, and $P(C_2H_5)_3(C_5H_{11})I$, which are decomposed by silver oxide, yielding powerfully alkaline liquids, containing the hydrates $P(C_2H_5)_3(CH_3)(OH)$, $P(C_2H_5)_4(OH)$, and $P(C_2H_5)_3(C_5H_{11})OH$, which in every respect resemble hydrate of tetrethyl ammonium and its homologues.

Trimethylphosphine, $C_3H_9P = P(CH_3)_3$. — This substance is very similar to the corresponding ethyl-base, but more volatile. When left in contact with atmospheric air, it forms an oxide which crystallizes in beautiful white needles. With iodide of methyl, ethyl, and amyl, it yields the iodides $P(CH_3)_4I$, $P(CH_3)_3(C_2H_5)I$, and $P(CH_3)_3(C_5H_{11})I$, from which three analogous hydrates may be produced by means of silver oxide.

ANTIMONY BASES or STIBINES.

Triethylstibine, or Stibethyl, $Sb(C_2H_5)_3$, is obtained by distilling ethyl iodide with an alloy of antimony and potassium. It is a transparent, very mobile liquid, having a penetrating odor of onions. It boils at 158° C. (316° F.). In contact with atmospheric air, it emits a dense white fume, and frequently even takes fire, burning with a white brilliant flame. It is analogous in many of its reactions to triethylamine, but has much more powerful combining tendencies, uniting readily with two atoms of chlorine, bromine, or iodine, and 1 atom of oxygen or sulphur, thereby forming compounds in which the antimony is quinquivalent, such as $Sb^v(C_2H_5)_3Cl_2$, $Sb^v(C_2H_5)_3O''$, &c. The same tendency to act as a bivalent-radical is, however, exhibited by triethylamine, which, though it does not unite directly with elementary bodies, can nevertheless take up a molecule of hydrogen chloride, ethyl iodide, &c., likewise producing compounds in which the nitrogen is quinquivalent, *e. g.*, $N^v(C_2H_5)_3HCl$, $N^v(C_2H_5)_3(C_2H_5)I$, &c.

Stibethyl oxide, $Sb(C_2H_5)_3O$, forms a viscid transparent mass, soluble in water and alcohol. It is extremely bitter and not poisonous. It cannot be volatilized without decomposition. It combines with acids, giving rise to crystallizable salts containing two equivalents of acid.

Stibethyl sulphide, $Sb(C_2H_5)_3S$. — Beautiful crystals of silvery lustre, soluble in water and alcohol. Their taste is bitter, and their odor similar to that of mercaptan. The solution of this compound exhibits the deportment of an alkaline sulphide: it precipitates metals from their solutions

as sulphides, a soluble salt of stibethyl being formed at the same time. This deportment, indeed, affords the simplest means of preparing the salts of stibethyl.

Stibethyl chloride, $Sb(C_2H_5)_3Cl_2$. — Colorless liquid having the odor of turpentine oil.

Stibethyl iodide, $Sb(C_2H_5)_3I_2$. — Colorless needles of intensely bitter taste.

The analogy of triethylstibine with triethylamine is best exhibited in its deportment with ethyl iodide. The two substances combine, forming a new iodide, containing $Sb(C_2H_5)_4I$, from which silver oxide separates a powerful alkaline base analogous to tetrethyl-ammonium hydrate:

$$N(C_2H_5)_4(OH) \qquad Sb(C_2H_5)_4OH.$$

A series of analogous substances exist in the methyl series. They have been examined by Landolt, who has described several of their compounds, and separated the methyl-antimony-base corresponding to tetramethyl-ammonium hydrate.

The *iodide*, $Sb(CH_3)_4I$, produced by the action of methyl iodide upon trimethylstibine, $Sb(CH_3)_3$, crystallizes in white six-sided tables, which are easily soluble in water and alcohol, and slightly soluble in ether. It has a very bitter taste, and is decomposed by the action of heat. When treated with silver oxide, it yields a powerfully alkaline solution, exhibiting all the properties of potash, from which, on evaporation, a white crystalline mass, the *hydrate of tetramethylstibonium*, $Sb(CH_3)_4(OH)$, crystallizes. This compound forms an acid salt with sulphuric acid, which crystallizes in tables. It contains $Sb(CH_3)_4HSO_4$.

ARSENIC BASES.

Triethylarsine, $As(C_2H_5)_3$, is produced by distilling an alloy of arsenic and sodium with ethyl iodide. At the same time, also, there is formed another body, containing $As_2(C_2H_5)_4$, analogous to arsendimethyl or cacodyl. Both compounds are liquids of powerful odor; they may be separated by distillation in an atmosphere of carbon-dioxide, the triethylarsine passing over last.

Triethylarsine may be obtained pure by a process analogous to that employed for the preparation of triethylphosphine, namely, by distilling arsenious chloride, $AsCl_3$, with zinc-ethyl. It is a colorless liquid of most disagreeable odor, similar to that of arsenetted hydrogen, soluble in water, alcohol, and ether, and boiling at 140°. Triethylarsine combines directly with oxygen, sulphur, bromine, and iodine, giving rise to a series of compounds containing 2 atoms of bromine or iodine, 1 atom of sulphur or oxygen, and analogous to the corresponding compounds of triethylstibine.

Triethylarsine submitted to the action of ethyl iodide yields a crystalline compound, $As(C_2H_5)_4I$, from which freshly precipitated silver oxide separates the corresponding hydrate, $As(C_2H_5)_4OH$, a powerfully alkaline substance, similar to the corresponding nitrogen-, phosphorus-, and antimony-compounds.

Analogous substances exist in the methyl series. Trimethylarsine, $As(CH_3)_3$, is formed, together with arsendimethyl or cacodyl, $As_2(CH_3)_4$, when an alloy of arsenic and sodium is submitted to the action of methyl iodide. It unites with methyl iodide, producing tetramethylarsonium iodide, $As(CH_3)_4I$, from which silver oxide separates the hydrate, $As(CH_3)_4OH$. The iodide just mentioned is formed, together with iodide of cacodyl, when cacodyl is acted upon by methyl iodide:

$$As_2(CH_3)_4 + 2CH_3I = As(CH_3)_4I + As(CH_3)_2I.$$

By substituting ethyl iodide for methyl iodide in this reaction, the compound $As(CH_3)_2(C_2H_5)_2I$ is formed. All these iodides, treated with moist silver oxide, yield the corresponding hydrates.

Arsendimethyl and arsenmonomethyl will be most conveniently described in this place, though they do not strictly belong to the ammonia type, at least when in the free state.

Arsendimethyl or **Cacodyl**, $As_2(CH_3)_4$, or $\begin{matrix} As'''(CH_3)_2 \\ | \\ As'''(CH_3)_2 \end{matrix}$. — The arsenic in this compound is still trivalent, one unit of equivalence of each of the arsenic-atoms being satisfied by combination with the other, just as in the solid hydrogen arsenide, As_2H_4 (p. 423). When, however, the arsendimethyl combines with chlorine or other monatomic radicals, the molecule splits into two; thus:

$$As(CH_3)_4 \quad + \quad Cl_2 \quad = \quad 2AS'''(CH_3)_2Cl.$$

Cacodyl, so called from its repulsive odor, constitutes, together with its products of oxidation, the spontaneously inflammable liquid known as *Cadet's fuming liquid*, or *Alkarsin*. This liquid is prepared by distilling potassium acetate with arsenious oxide. Equal weights of these two substances, both well dried, are intimately mixed and introduced into a glass retort connected with a condenser and tubulated receiver cooled by ice, a tube being attached to the receiver to carry away the permanently gaseous products to some distance from the experimenter. Heat is then applied to the retort, which is gradually increased to redness. At the close of the operation, the receiver is found to contain two liquids, besides a quantity of reduced arsenic: the heavier of these is the crude cacodyl; the other consists chiefly of water, acetic acid, and acetone. The gas given off during the distillation is principally carbon dioxide. The crude cacodyl is repeatedly washed by agitation with water previously freed from air by boiling, and afterwards redistilled from potassium hydrate in a vessel filled with pure hydrogen gas. All these operations must be conducted in the open air.

Pure cacodyl is obtained by decomposing the chloride with metallic zinc, dissolving out the zinc chloride with water, and dehydrating the oily liquid with calcium chloride. The strong tendency of cacodyl to take fire in the air, and the extremely poisonous character of its vapors, render it necessary to perform all the distillations in sealed vessels filled with dry carbon dioxide. Bunsen, to whose skill and perseverance we are indebted for the discovery of this remarkable compound, proceeds as follows:

1. A dilute alcoholic solution of alkarsin is cautiously mixed with an equally dilute solution of mercuric chloride, avoiding an excess of the latter; a white crystalline, inodorous precipitate then falls, containing $As_2(CH_3)_4O \cdot HgCl_2$: when this is distilled with concentrated hydrochloric acid, it yields mercuric chloride, water, and *cacodyl chloride*, which distils over. The product is left for some time in contact with calcium chloride and a little quicklime, and then distilled alone in an atmosphere of carbon dioxide.

2. To obtain free cacodyl, the pure anhydrous chloride is digested for three hours at a temperature of 100° with slips of clean metallic zinc contained in a bulb blown upon a glass tube previously filled with carbonic acid gas, and hermetically sealed. The metal dissolves quietly without evolution of gas. When the action is complete, and the whole cool, the vessel is observed to contain a white saline mass, which, on the admission of a little water, dissolves, and liberates a heavy oily liquid, the cacodyl itself. This is rendered quite pure by distillation from a fresh quantity of zinc, the process being conducted in the little apparatus shown in

fig. 196, which is made from a piece of glass tube, and is intended to serve the purpose both of retort and receiver. The zinc is introduced into the upper bulb, and the tube drawn out in the manner represented. The whole is then filled with carbon dioxide, and the lower extremity put into communication with a little hand-syringe. On dipping the point *a* into the crude cacodyl, and making a slight movement of exhaustion, the liquid is drawn up into the bulb. Both extremities are then sealed in the blowpipe flame, and after a short digestion at 100°, or a little above, the pure cacodyl is distilled off into the lower bulb, which is kept cool. It forms a colorless, transparent, thin liquid, much resembling alkarsin in odor, and surpassing that substance in inflammability. When poured into the air, or into oxygen gas, it ignites instantly: the same thing happens with chlorine. With very limited access of air it throws off white fumes, passing into oxide, and eventually into cacodylic acid. Cacodyl boils at 170° C. (338° F.), and when cooled to —6° C. (21° F.), crystallizes in large, transparent, square prisms. It combines directly also with sulphur.

Fig. 196.

Cacodyl is decomposed at a temperature below redness into metallic arsenic, and a mixture of 2 measures of marsh-gas and 1 measure of ethene gas.

The powerful combining tendencies of cacodyl indicate that it is an unsaturated compound: it can, in fact, take up 2 atoms of a monad or 1 atom of a dyad element, forming compounds like the chloride, $As_2(CH_3)_4Cl_2 = 2As(CH_3)_2Cl$, and the oxide, $As_2(CH_3)_4O$, in which the arsenic is trivalent; or again, 6 atoms of a monad or 3 atoms of a dyad element, forming compounds like the trichloride, $As_2(CH_3)_4Cl_6 = 2As(CH_3)_2Cl_3$, in which arsenic is quinquivalent. These last-mentioned bodies are the most stable of all the cacodyl compounds.

Cacodyl Chloride, or Arsen-chlorodimethide, $As'''(CH_3)_2Cl$, prepared as above described, is a colorless liquid, which does not fume in the air, but emits an intensely poisonous vapor. It is heavier than water, and insoluble in that liquid, as also in ether; alcohol, on the other hand, dissolves it with facility. The boiling point of this compound is a little above 100°; its vapor is colorless, spontaneously inflammable in the air, and has a density of 4·56. Dilute nitric acid dissolves the chloride without change; with the concentrated acid, ignition and explosion occur. Cacodyl chloride combines with cuprous chloride, forming a white, insoluble, crystalline double salt, containing $As_2(CH_3)_4Cl_2 . Cu'_2Cl_2$; also with cacodyl oxide.

Cacodyl chloride forms a hydrate which is thick, viscid, and readily dehydrated by calcium chloride.

Cacodyltrichloride, $As^v(CH_3)_2Cl_3$, is produced by the action of phosphorus pentachloride on cacodylic acid:

$$As^v(CH_3)_2O''(OH) + 2PCl_5 = As(CH_3)_2Cl_3 + 2POCl_3 + HCl.$$

Also by the action of chlorine gas on the monochloride. Prepared by the first method, it forms splendid large prismatic crystals, which however are very unstable, being instantly decomposed, at temperatures between 40° and 50° C. (104–122° F.), into methyl chloride and arsen-monomethyl chloride:

$$As^v(CH_3)_2Cl_3 = CH_3Cl + As'''(CH_3)Cl_2.$$

Cacodyl Iodide, $As(CH_3)_2I$, is a thin, yellowish liquid, of offensive odor, and considerable specific gravity, prepared by distilling alkarsin with

strong solution of hydriodic acid. A yellow crystalline substance is formed at the same time, which is an oxyiodide. *Cacodyl bromide* and *fluoride* have also been obtained.

Cacodyl Cyanide, $As(CH_3)_2CN$, is easily formed by distilling alkarsin with strong hydrocyanic acid, or mercuric cyanide. Above 32·7° C. (90° F.), it is a colorless, ethereal liquid, but below that temperature it crystallizes in colorless four-sided prisms, of beautiful diamond lustre. It boils at about 140° C. (284° F.), and is but slightly soluble in water. It requires to be heated before inflammation occurs. The vapor of this substance is most fearfully poisonous: the atmosphere of a room is said to be so far contaminated by the evaporation of a few grains of it as to cause instantaneous numbness of the hands and feet, vertigo, and even unconsciousness.

Cacodyl Oxide, $As'''_2(CH_3)_4O''$.—This compound is formed by the slow oxidation of cacodyl. When air is allowed access to an aqueous solution of alkarsin, so slowly that no sensible rise of temperature follows, that body is gradually converted into a thick, syrupy liquid, full of crystals of cacodylic acid. On dissolving this mass in water, and distilling, water having the odor of alkarsin passes over, and afterward an oily liquid, which is the cacodyl oxide. Impure cacodylic acid remains in the retort.

Cacodyl oxide, purified by rectification from caustic baryta, is a colorless, oily liquid, having a pungent odor, sparingly soluble in water, and boiling at 120° C. (248° F.), strongly resembling alkarsin in odor, in its relations to solvents, and in the greater number of its reactions; but it neither fumes in the air, nor takes fire at common temperatures: its vapor mixed with air, and heated to about 88° C. (190° F.), explodes with violence. It dissolves in hydrochloric, hydrobromic, and hydriodic acids, forming chloride, bromide, and iodide of cacodyl.

Cacodyl dioxide, $As_2(CH_3)_4O_2$, is the thick syrupy liquid produced by the slow oxidation of cacodyl or of alkarsin. It is decomposed by water, and then yields a distillate of cacodyl monoxide, with a residue of cacodylic acid:

$$2As_2(CH_3)_4O_2 + H_2O = As_2(CH_3)_4O + 2As(CH_3)_2O(OH.)$$

Cacodylic Acid, $As^v(CH_3)_2O''(OH)$, also called *Alkargen*.—This is the ultimate product of the action of oxygen at a low temperature upon cacodyl or alkarsin in presence of water: it is best prepared by adding mercuric oxide to alkarsin, covered with a layer of water and artificially cooled, until the mixture loses all odor, and afterward decomposing any mercuric cacodylate that may have been formed, by the cautious addition of more alkarsin. The liquid yields, by evaporation to dryness and solution in alcohol, crystals of cacodylic acid. The sulphide and other compounds of cacodyl yield the same substance on exposure to air. Cacodylic acid forms brilliant, colorless, brittle crystals, which have the form of a modified square prism: it is permanent in dry air, but deliquescent in a moist atmosphere. It is not at all poisonous, though it contains more than 50 per cent. of arsenic. It is very soluble in water and in alcohol, but not in ether: the solution has an acid reaction. When mixed with alkalies and evaporated, it leaves a gummy, amorphous mass. With the oxides of silver and mercury, on the other hand, it yields crystallizable compounds. It unites with cacodyl oxide, and forms a variety of combinations with metallic salts. Cacodylic acid is exceedingly stable: it is not affected by red fuming nitric acid, nitromuriatic acid, or even chromic acid in solution: it may be boiled with these substances without the least change. It is deoxidized, however, by phosphorous acid and stannous chloride, yielding cacodyl oxide. Dry hydriodic acid gas decomposes it, with production of water, cacodyl iodide,

and free iodine. With dry hydrochloric acid gas, or with the concentrated aqueous acid, cacodylic acid unites directly, forming the compound $As(CH_3)_2O_2H.HCl$. But by exposing cacodylic acid for a long time to a stream of hydrochloric acid gas, *arsen-monomethyl dichloride* is obtained, together with water and methyl chloride:

$$As(CH_3)_2O_2H + 3HCl = As(CH_3)Cl_2 + 2H_2O + CH_3Cl.$$

Phosphorus pentachloride converts cacodylic acid into cacodyl trichloride (p. 764).

Cacodyl Sulphide, $As_2(CH_3)_4S$, is formed by adding barium sulphide to crude cacodyl, or by distilling barium sulph-hydrate with cacodyl chloride. It is a transparent liquid which retains its fluidity at —40°, and boils at a temperature considerably above 100°.

Cacodyl disulphide, $As_2(CH_3)_4S_2$, is formed by the action of sulphur on cacodyl or the monosulphide, or by treating cacodylic acid with sulphuretted hydrogen in a vessel externally cooled. It separates from the solution in large rhombic crystals. The alcoholic solution of this compound yields with various metallic solutions, precipitates consisting of salts of *sulphocacodylic acid*, $As(CH_3)_2S_2H$, analogous to cacodylic acid. The lead-salt, $As_2(CH_3)_4S_4Pb''$, forms small white crystals.

Arsenmonomethyl, $As(CH_3)$. — This radical, which is not known in the separate state, is either bivalent or quadrivalent. Its dichloride, $As'''(CH_3)Cl_2$, is produced either by the decomposition of cacodyl trichloride by heat: $As(CH_3)_2Cl_3 = As(CH_3)Cl_2 + CH_3Cl$; or by the prolonged action of hydrochloric acid on cacodylic acid (p. 765). It is a colorless, heavy, mobile liquid, having a strong reducing power; boils at 133° C. (271° F.). Its vapor exerts a most violent action on the mucous membranes; on smelling it, the eyes, nose, and whole face swell up, and a peculiar lancinating pain is felt, extending down to the throat. The *tetrachloride*, $As^v(CH_3)Cl_4$, is obtained in large crystals by passing chlorine over a mixture of the dichloride and carbon bisulphide cooled to —10°. It is very unstable, decomposing even near 0° into methyl chloride and arsenious chloride, $AsCl_3$. There is also a chlorobromide, $As(CH_3)ClBr$, and a di-iodide, $As(CH_3)I_2$.

The *oxide*, $As(CH_3)O$, obtained by decomposing the dichloride with potassium carbonate, forms large cubical crystals, soluble in water, alcohol, and ether, and resolved by distillation with potash into arsenious oxide and cacodyl oxide: $4As(CH_3)O = As_2O_3 + As_2(CH_3)_4O$.

Arsenmethylic Acid, $As^v(CH_3)O''(OH)_2$, is obtained as a barium-salt by decomposing arsenmethyl dichloride with a slight excess of silver-oxide; and this salt, decomposed by sulphuric acid, yields the acid which remains on evaporation in the form of a laminated mass. It is bibasic.

Arsenmethyl sulphide, $As(CH_3)S$, is obtained as a white mass by passing hydrogen sulphide over the dichloride.

On comparing the combining or equivalent values of the several arsenides of methyl, it will be seen that they all unite with elementary bodies and compound radicals, in such proportion as to form compounds in which the arsenic is either trivalent or quinquivalent, the last-mentioned compounds being by far the most stable. Thus:

Arsenmonomethyl, $As(CH_3)$, is bi- and quadri-valent, forming the chlorides $As'''(CH_3)Cl_2$ and $As^v(CH_3)Cl_4$.

Arsendimethyl, $As(CH_3)_2$, is mono- and tri-valent, forming the chlorides $As'''(CH_3)_2Cl$ and $As^v(CH_3)_2Cl_3$.

Arsentrimethyl, $As(CH_3)_3$, is bivalent only, and forms the chloride $As^v(CH_3)_3Cl_2$.

Arsenmethylium, or Tetramethylarsonium, $As(CH_3)_4$, is univalent, forming the chloride $As^v(CH_3)_4Cl$.

Bismethyl or **Triethylbismuthine**, $Bi(C_2H_5)_3$, analogous in composition to triethylstibine and triethylarsine, is formed by the action of ethyl iodide on an alloy of bismuth and potassium, and is extracted from the residue by ether. It is a yellow liquid of specific gravity 1·82, has a most nauseous odor, and emits vapors which take fire in contact with the air. It unites with oxygen, chlorine, bromine, iodine, and nitric acid.

Borethyl, $B(C_2H_5)_3$. — Dr. Frankland has obtained this compound by treating boric ether with zinc-ethyl: it is a colorless mobile liquid having a pungent odor, irritating the eyes, of sp. gr. 0·696, and boiling at 95° C. (203° F.). Borethyl is insoluble in water, but very slowly decomposed when left in prolonged contact with it. When exposed to the air it is spontaneously inflamed, burning with a beautiful green and somewhat smoky flame. It combines with ammonia, forming the compound $NH_3 . B(C_2H_5)_3$. By the gradual action of dry air, and, ultimately, of dry oxygen, borethyl is converted into an oxygen-compound of the formula $B(C_2H_5)_3O_2$.

DIATOMIC BASES OF THE PHOSPHORUS AND ARSENIC SERIES.

The action of ethene bromide on triethylphosphine gives rise to the formation of two crystalline bromides, according to the proportions in which the substances are brought in contact. These bromides are $C_8H_{19}PBr_2 = C_6H_{15}P + C_2H_4Br_2$ and $C_{14}H_{34}P_2Br_2 = 2C_6H_{15}P + C_2H_4Br_2$. The first of these compounds is the bromide of a phosphonium in which 3 atoms of hydrogen are replaced by ethyl and one atom by the univalent radical bromethyl, C_2H_4Br, thus $[(C_2H_4Br)(C_2H_5)_3P]Br$. Half the bromine in this salt is unaffected by the action of silver-salts; it may accordingly be designated as *bromide of bromethyl-triethyl-phosphonium*. Numerous salts of this compound are known, but the free base cannot be obtained, since silver oxide eliminates the latent bromine, giving rise to the formation of a base containing $[(C_2H_5O)(C_2H_5)_3P]OH$. The second compound is the dibromide of *ethene-hexethyl-diphosphonium*, $[(C_2H_4)''(C_2H_5)_6P_2]''Br_2$. This radical, which corresponds to 2 equivalents of ammonium, $2NH_4 = N_2H_8$, forms a series of very stable and beautiful salts, especially an iodide which is difficultly soluble in water. In all these salts the base, which is composed of 1 molecule of ethene, 6 molecules of ethyl, and 2 atoms of phosphorus, is united with 2 molecules of univalent-acid radical; the platinum-salt contains $(C_2H_4)''(C_2H_5)_6P_2Br_2 . Pt^{iv}Cl_4$. The free, very caustic, and stable base has the composition $[(C_2H_4)''(C_2H_5)_6P_2]''(OH)_2$.

The dibromide of ethene-hexethyl-diphosphonium may be formed by the action of triethylphosphine upon the brominated bromide which has been mentioned as the first product of the action of ethene dibromide upon triethylphosphine: $C_3H_{19}PBr_2 + C_6H_{15}P = C_{14}H_{34}P_2Br_2$. If the triethylphosphine be replaced in this process by ammonia or by monamines in general, or by monarsines, an almost unlimited series of diatomic salts may be formed, in which phosphorus and nitrogen or phosphorus and arsenic are associated.

Thus the action of ammonia, of ethylamine, and of triethylarsine, gives rise respectively to the following compounds:

Dibromide of Ethene-triethyl-phosphammonium . .	$[(C_2H_4)''(C_2H_5)_3H_3PN]''Br_2$.
Dibromide of Ethene-tetrethyl phosphammonium . .	$[(C_2H_4)''(C_2H_5)_4H_2PN]''Br_2$.
Dibromide of Ethene-hexethyl-phospharsonium . .	$[(C_2H_4)''(C_2H_5)_6PAs]''Br$.

Treated with silver oxide, these bromides yield the very caustic diatomic bases —

Hydrate of Ethene-triethyl-phosphammonium . .	$[(C_2H_4)''(C_2H_5)_3H_3PN]''(OH)_2$.
Hydrate of Ethene-tetrethyl-phosphammonium . .	$[(C_2H_4)''(C_2H_5)_4H_2PN]''(OH)_2$.
Hydrate of Ethene-hexethyl-phosparsonium . .	$[(C_2H_4)''(C_2H_5)_6PAs]''(OH)_2$.

The arsenic bases, when submitted to the action of ethene dibromide, give rise to perfectly analogous results. The limits of this Manual will not permit us to examine these remarkable compounds in detail.

IV. — Compounds of Alcohol-radicals with Bivalent and Quadrivalent Metals and Metalloids.

The bodies of this group which contain bivalent elements, such as zinc, are saturated compounds, not capable of uniting directly with chlorine, oxygen, &c.; those which contain quadrivalent metals, like tin, are saturated or unsaturated accordingly as they contain four or only two equivalents of alcohol-radicals.

All these compounds are frequently designated as *organo-metallic bodies*, a term likewise including the compounds of alcohol-radicals with arsenic, antimony, and bismuth. We shall describe chiefly the ethyl compounds, to which the methyl and amyl compounds are strictly analogous.

Zinc-ethyl or **Zinc ethide**, $Zn''(C_2H_5)_2$. — This compound, discovered by Frankland, is formed, together with zinc-iodide, when ethyl iodide is heated with metallic zinc in a sealed glass tube, or, for larger quantities, in a strong and well-closed copper cylinder: $2C_2H_5I + Zn_2 = ZnI_2 + Zn(C_2H_5)_2$. The two products remain combined together in the form of a white crystalline mass, from which the zinc-ethyl may be separated by distillation in an atmosphere of hydrogen. It is a mobile and very volatile liquid, having a disagreeable odor, taking fire instantly on coming in contact with the air, and diffusing white fumes of zinc oxide. Water decomposes it violently, with formation of zinc hydrate, and evolution of ethane or ethyl-hydride: $Zn(C_2H_5)_2 + 2H_2O = ZnH_2O_2 + C_2H_6$. When gradually mixed with dry *oxygen*, it passes through two stages of oxidation, yielding first zinc ethyl-ethylate, $Zn''\left\{\begin{matrix}C_2H_5\\OC_2H_5\end{matrix}\right.$, and finally zinc ethylate, $Zn''(OC_2H_5)_2$. With iodine and other halogens, the reaction also takes place by two stages, but consists in the successive substitution of the halogen for the ethyl; thus:

$$Zn(C_2H_5)_2 + I_2 = C_2H_5I + Zn(C_2H_5)I,$$

and

$$Zn(C_2H_5)I + I_2 = C_2H_5I + ZnI_2.$$

Zinc ethide has become a very important reagent in organic chemistry, serving to effect the substitution of the positive radical ethyl for chlorine, iodine, and other negative elements, and thus enabling us to build up carbon-compounds from others lower in the scale. Many examples of these reactions have already been given in the chapters on alcohols and acids. In like manner it serves for the preparation of many other organo-metallic bodies. The following equations exhibit the mode of formation of mercuric methide, stannic ethide, and triethylarsine by means of zinc ethide:

$$Zn''(C_2H_5)_2 + Hg''Cl_2 = ZnCl_2 + Hg''(C_2H_5)_2$$
$$2Zn''(C_2H_5)_2 + Sn^{iv}Cl_4 = 2ZnCl_2 + Sn^{iv}(C_2H_5)_4$$
$$3Zn''(C_2H_5)_2 + 2As'''Cl_3 = 3ZnCl_2 + 2As'''(C_2H_5)_3.$$

Zinc Methide, $Zn''(CH_3)$, is analogous in its reactions to zinc ethide, but is still more volatile and inflammable.

Potassium Ethide, C_2H_5K, and **Sodium Ethide**, C_2H_5Na, are not known in the separate state, but only in combination with zinc-ethyl. These mixed compounds are produced by the action of potassium on sodium zinc-ethyl; thus:

$$3Zn(C_2H_5)_2 + Na_2 = Zn + 2(C_2H_5)_3\left\{\begin{matrix}Zn''\\K.\end{matrix}\right.$$

These compounds and their homologues, discovered by Wanklyn, have also played an important part in chemical synthesis. The production of the fatty acids by the combination of carbon dioxide with sodium ethide, &c. has been frequently mentioned.

Mercuric Ethide, $Hg''(C_2H_5)_2$. — This compound is formed, as already observed, by the action of mercuric chloride on zinc ethide, but it is more easily prepared by the action of sodium-amalgam on ethyl iodide in presence of acetic ether:

$$2C_2H_5I + Na_2 + Hg = 2NaI + Hg(C_2H_5)_2.$$

The acetic ether takes no part in the reaction; nevertheless its presence appears to be essential.

Mercuric ethide is a transparent, colorless liquid, boiling at 159°. It burns with a smoky flame, giving off a large quantity of mercurial vapor. Chlorine, bromine, and iodine remove one equivalent of ethyl from this compound, and take its place, forming mercuric chlorethide, &c.; thus:

$$Hg(C_2H_5)_2 + Cl_2 = C_2H_5Cl + Hg(C_2H_5)Cl.$$

A similar action is exerted by acids, *e. g.*, by hydrobromic acid, the products being ethane and mercuric bromethide:

$$Hg(C_2H_5)_2 + HBr = C_2H_6 + Hg(C_2H_5)Br.$$

The chlorethide or bromethide is converted by water into mercuric ethylhydrate, $Hg''(C_2H_5)(OH)$. Mercuric ethide serves for the preparation of several other organo-metallic bodies.

Aluminium Methide, $Al'''(CH_3)_3$, or $Al_2(CH_3)_6$. — This compound, discovered by Buckton and Odling,* is formed by heating mercuric ethide with aluminium. It is a mobile liquid, which crystallizes at a little above 0°, and boils at 130° C. (266° F.). At and above 220° C. (428° F.) the density of its vapor, compared with that of air, is 2·8, which is near to the theoretical density calculated for the formula $Al(C_2H_5)_3$, namely, 2·5. This seems to show that the true formula of the compound is $Al(C_2H_5)_3$, and not $Al_2(C_2H_5)_6$, and, consequently, that aluminium is a triad, not a tetrad (p. 333). At temperatures near the boiling point, however, the vapor-density becomes 4·4, approximating to the theoretical density calculated for the formula $Al_2(C_2H_5)_6$.

Aluminium ethide resembles the methyl compound. It boils at 194° C. (381° F.), and its vapor likewise exhibits, at temperatures considerably above its boiling point, a density nearly equal to that required by the formula $Al(C_2H_5)_3$, for a two-volume condensation.†

* Proceedings of the Royal Society, xiv. 19.

† The vapor-density of aluminium chloride, as determined by Deville, agrees with that required by the formula Al_2Cl_6; but as this compound has a very high boiling point, it was perhaps not heated sufficiently to convert it into a perfect gas (see page 461).

Ethyl Compounds of Tin. — Tin forms two ethyl compounds, $Sn''(C_2H_5)_2$ and $Sn^{iv}(C_2H_5)_4$, analogous to stannous and stannic chloride; also a stannoso-stannous ethide, $Sn_2(C_2H_5)_6$, analogous in constitution to ethane, C_2H_6. Stannic ethide is a saturated compound, but the other two are unsaturated bodies, capable of uniting with chlorine, bromine, oxygen, and acid radicals, and being thereby converted into compounds of the stannic type.

Stannous Ethide, $Sn''(C_2H_5)_2$. — When ethyl iodide and tinfoil are heated together in a sealed glass tube to about 150° or 180° C. (302°–356° F.), stannous iodethide, $Sn^{iv}(C_2H_5)_2I_2$, is produced, crystallizing in colorless needles. The same compound is obtained when tin and ethyl iodide are exposed to the rays of the sun concentrated by a parabolic reflector. The reaction is considerably facilitated if the tin be alloyed by one-tenth of its weight of sodium. This iodide is decomposed by sodium or zinc, which abstracts the iodine and leaves stannous ethide in the form of a thick, oily liquid, insoluble in water, and having the sp. gr. 1·55. Stannous ethide combines directly with 2 atoms of chlorine, iodine, and bromine, forming stannic chlorethide, $Sn^{iv}(C_2H_5)_2Cl_2$, &c, Exposed to the air, it absorbs oxygen and is converted into stannous oxethide, $Sn^{iv}(C_2H_5)_2O$, a whitish, tasteless, inodorous powder, which, when treated with oxygen-acids, yields well crystallized stannous salts, such as $Sn^{iv}(C_2H_5)_2(NO_3)_2$, $Sn^{iv}(C_2H_5)_2SO_4$, &c.

Stannoso-stannic Ethide, $Sn_2(C_2H_5)_6$, is always produced in small quantity when stannous ethide is prepared by the methods above mentioned. It is really obtained in the free state by digesting an alloy of 1 part of sodium and 5 parts of tin with ethyl iodide, exhausting the mass with ether, evaporating the ethereal solution, and exhausting the residue with alcohol. The stannoso-stannic ethide, being insoluble in that liquid, then remains behind. It is a yellow oil, boiling at 180° C. (356° F.), combining directly with chlorine, bromine, and iodine to form two molecules of a stannic compound; *e. g.:*

$$Sn_2(C_2H_5)_6 + Cl_2 = 2Sn^{iv}(C_2H_5)_3Cl;$$
Stannic chloro-triethide.

also with oxygen, forming distannic oxy-hexethide, $Sn^{iv}{}_2(C_2H_5)_6O$. This oxide is, however, best obtained by distilling stannous oxy-diethide, $Sn^{iv}(C_2H_5)_2O$ (above described), with potash. It is an oily liquid, soluble in alcohol, ether, and water; the aqueous solution has a strong alkaline reaction. It is easily acted upon by oxygen-acids, yielding the corresponding sulphate, $Sn_2(C_2H_5)_6SO_4$, &c.

Stannic Ethide, $Sn^{iv}(C_2H_5)_4$, is produced by the action of zinc ethide on stannic chloride; also by the distillation of stannous ethide, $2Sn(C_2H_5)_2 = Sn + Sn(C_2H_5)_4$. It is a colorless, nearly odorless liquid, of sp. gr. 1·19, boiling at 181° C. (358° F.), and very inflammable, burning with a highly luminous flame. When treated with chlorine, bromine, &c., or with acids, it forms substitution-products: thus, with iodine, it splits up into ethyl iodide and stannic iodotriethide:

$$Sn(C_2H_5)_4 + I_2 = C_2H_5I + Sn(C_2H_5)_3I.$$

With strong hydrochloric acid, it yields ethane and stannic chlorotriethide, $Sn(C_2H_5)_4 + HCl = C_2H_6 + Sn(C_2H_5)_3Cl$.

Plumbic Ethide, $Pb(C_2H_5)_4$, is produced by the action of plumbic chloride on zinc ethide:

$$2Zn(C_2H_5)_2 + 2PbCl_2 = 2ZnCl_2 + Pb + Pb(C_2H_5)_4.$$

It is a colorless limpid liquid, soluble in ether but not in water. It is not acted upon by oxygen at ordinary temperatures; but chlorine, bromine,

and iodine act violently upon it, in the same manner as on stannic ethide, forming plumbic chloro-triethide, $Pb(C_2H_5)_3Cl$, &c. Plumbic ethide is interesting, as affording a proof that lead is really a tetrad (p. 398.)

Tellurethyl, $Te''(C_2H_5)_2$, is obtained by distilling potassium telluride with potassium ethylsulphate. It is a heavy, oily liquid of yellowish-red color, very inflammable, and having a most insufferable odor. It acts as a bivalent radical, uniting directly with chlorine, bromine, oxygen, &c., to form compounds in which the tellurium enters as a tetrad, *e. g.*, $Te^{iv}(C_2H_5)_2Cl_2$, $Te^{iv}(C_2H_5)_2O''$, &c. The nitrate $Te(C_2H_5)_2(NO_3)_2$, is obtained by treating tellethuryl with nitric acid; the other salts by double decomposition; the chloride, for example, settles down, as a heavy oil, on adding hydrochloric acid to a solution of the nitrate. The oxide is best prepared by treating the chloride with water and silver oxide. It dissolves in water, forming a slightly alkaline liquid.

Telluro-methyl, $Te(CH_3)_2$, and *telluramyl*, $Te(C_5H_{11})_2$, are similar in their properties to tellurethyl. The corresponding *selenium compounds* have likewise been obtained.

There are also compounds of *sulphur* with alcohol-radicals in which the sulphur plays the part of a quadrivalent element, viz., the *triethylsulphurous compounds*, already described (p. 530).—*Sulphurous iodo-triethide*, $S^{iv}(C_2H_5)_3I$, for example, is produced by combination of ethyl monosulphide, $S(C_2H_5)_2$, with ethyl iodide, C_2H_5I.

Other compounds, in which the sulphur may be regarded as a hexad, are obtained by combining ethyl sulphide and ethene sulphide with ethene dibromide: thus *sulphuric diethene-dibromide*, $S^{iv}(C_2H_4)''_2Br_2$, is formed by combination of $S(C_2H_4)$ with $C_2H_4Br_2$, and *sulphuric diethyl-ethene-dibromide*, $S^{vi}(C_2H_5)_2(C_2H_4)''Br_2$, in like manner by combination of $S(C_2H_5)_2$ with $C_2H_4Br_2$.

AMIDES.

We have had frequent occasion to speak of these compounds, as derived from ammonium-salts by abstraction of water, or from acids by substitution of amidogen, NH_2, for hydroxyl, OH, or from one or more molecules of ammonia by substitution of acid-radicals for hydrogen. They are divided (like amines) into monamides, diamides, and triamides, each of which groups is further subdivided into primary, secondary, and tertiary amides, accordingly as one-third, two-thirds, or the whole of the hydrogen is replaced by acid-radicals. If the hydrogen is replaced partly by acid-radicals, and partly by alcohol-radicals, the compound is called an *alkalamide*; for example, ethylacetamide, $NH(C_2H_5)(C_2H_3O)$; ethyldiacetamide, $N(C_2H_5)(C_2H_3O)_2$.

AMIDES DERIVED FROM MONATOMIC ACIDS.

A monatomic acid yields but one *primary amide*, which may be formed: 1. From its ammonium-salt by abstraction of a molecule of water, under the influence of heat; thus:

$$\underset{\text{Ammonium acetate.}}{C_2H_3(NH_4)O_2} - H_2O = \underset{\text{Acetamide.}}{C_2H_5NO} = \begin{matrix} CH_3 \\ | \\ CONH_2 \end{matrix} = N\left\{\begin{matrix} C_2H_3O \\ H_2 \end{matrix}\right.$$

These amides are also produced: 2. By the action of ammonia on acid chlorides; *e. g.:*

$$C_2H_3OCl + NH_3 = HCl + NH_2(C_2H_3O).$$

This method is especially adapted to the preparation of those amides which are insoluble in water.

3. By the action of ammonia on compound ethers:

$$\underset{\text{Ethyl acetate.}}{C_2H_3O.OC_2H_5} + NH_3 = \underset{\text{Ethyl alcohol.}}{HOC_2H_5} + \underset{\text{Acetamide.}}{NH_2(C_2H_3O)}.$$

Acetamide, which may be regarded as a type of primary monamides, is a white crystalline solid melting at 78° C. (172° F.), and boiling at 221° or 222° C. (430° F.). When heated with acids or with alkalies, it takes up water and is converted into acetic acid and ammonia. Distilled with phosphoric oxide, it gives up water and is converted into *acetonitrile* or *methyl cyanide*, $C_2H_5NO_2 - H_2O = C_2H_3N$. Heated in a stream of dry hydrochloric acid, it yields *diacetamide*, together with other products:

$$2NH_2(C_2H_3O) + HCl = NH_4Cl + NH(C_2H_3O)_2.$$

Acetamide acts both as a base and as an acid, combining with hydrochloric and with nitric acid, and likewise forming salts in which one atom of its hydrogen is replaced by a metal: *silver-acetamide*, C_2H_4NAgO, for example, is obtained in crystalline scales by saturating an aqueous solution of acetamide with silver oxide.

Benzamide, $C_7H_7NO = NH_2(C_7H_5O)$, is produced by methods similar to those above given for the formation of acetamide; also by oxidizing hippuric acid with lead dioxide:

$$C_9H_9NO_3 + O_2 = C_7H_7NCl + 2CO_2 + H_2O$$

Benzamide is a crystalline substance nearly insoluble in cold water, easily soluble in boiling water, also in alcohol and ether; it melts at 115° C. (239° F.), and volatilizes undecomposed between 286° and 290° C. (547°–554° F.). Its reactions are for the most part similar to those of acetamide. Heated with benzoic oxide or chloride, it yields benzonitrile and benzoic acid:

$$\underset{\text{Benzamide.}}{C_7H_7NO} + \underset{\text{Benzoic oxide.}}{(C_7H_5O)_2O} = \underset{\text{Benzonitrile.}}{C_7H_5N} + \underset{\text{Benzoic acid.}}{2C_7H_6O_2}$$

$$\underset{\text{Benzamide.}}{C_7H_7NO} + \underset{\text{Benzoic chloride.}}{C_7H_5OCl} = \underset{\text{Benzonitrile.}}{C_7H_5N} + \underset{\text{Benzoic acid.}}{C_7H_6O_2} + HCl$$

Heated with fuming hydrochloric acid, it forms hydrochloride of benzamide, $C_7H_7NO \cdot HCl$, which separates on cooling in long aggregated prisms. Its aqueous solution dissolves mercuric oxide, forming *benzomercuramide*, $N_2H_2(C_7H_5O)_2Hg''$.

Secondary monamides are those in which two atoms of hydrogen in a molecule of ammonia are replaced by two univalent or one bivalent acid-radical, or by one acid-radical and one alcohol-radical. Those containing only univalent radicals are formed by the action of dry hydrochloric acid gas on primary monamides at a high temperature; *e. g.*:

$$\underset{\text{Acetamide.}}{2NH_2(C_2H_3O)} + HCl = NH_4Cl + \underset{\text{Diacetamide.}}{NH(C_2H_3O)_2}$$

Those containing bivalent acid-radicals are called *imides*; *e. g*, succinimides, $NH(C_4H_4O_2)''$. They are derived from bibasic acids, and will be noticed farther on.

Secondary monamides (*alkalamides*) containing an acid-radical and an alcohol-radical, are formed by processes similar to those above given for the formation of the primary monamides, substituting amines for ammonia; thus:

$$\underset{\text{Ethylamine.}}{NH_2(C_2H_5)} + \underset{\text{Acetic chloride.}}{C_2H_3OCl} = HCl + \underset{\text{Ethyl-acetamide.}}{NH(C_2H_5)(C_2H_3O)}$$

$$\underset{\text{Ethylamine.}}{NH_2(C_2H_5)} + \underset{\text{Ethyl acetate.}}{C_2H_3O(OC_2H_5)} = \underset{\text{Alcohol.}}{HOC_2H_5} + \underset{\text{Ethyl-acetamide.}}{NH(C_2H_5)(C_2H_3O)}$$

They are crystalline, and for the most part do not combine with acids. When boiled with acids or alkalies, they take up water and regenerate their acid and primary amine; thus:

$$\underset{\text{Phenyl-acetamide.}}{NH(C_6H_5)(C_2H_3O)} + HOH = \underset{\text{Acetic acid.}}{C_2H_3O(OH)} + \underset{\text{Aniline.}}{NH_2(C_6H_5)}$$

Tertiary monamides are those in which the whole of the hydrogen in one molecule of ammonia is replaced by acid-radicals or by acid- and alcohol-radicals. Those of the latter kind, called tertiary alkalamides, are produced by the action of acid chlorides on secondary alkalamides:

$$\underset{\text{Phenyl-benzamide.}}{NH(C_6H_5)(C_7H_5O)} + \underset{\text{Benzoyl chloride.}}{C_7H_5OCl} = HCl + \underset{\text{Phenyl-dibenzamide.}}{N(C_6H_5)(C_7H_5O)_2}$$

Or by the action of monatomic acid oxides on cyanic ethers; *e. g.*:

$$\underset{\text{Acetic oxide.}}{(C_2H_3O)_2O} + \underset{\text{Ethyl cyanate.}}{N(CO)''(C_2H_5)} = CO_2 + \underset{\text{Ethyl-diacetamide.}}{N(C_2H_5)(C_2H_3O)_2}$$

AMIDES DERIVED FROM DIATOMIC AND MONOBASIC ACIDS.

Acids of this group may give rise to two monamides, both formed by substitution of one equivalent of NH_2 for OH, and therefore having the same composition. They are however isomeric, not identical, the one formed by replacement of the alcoholic hydroxyl being acid, while the other, formed by replacement of the basic hydroxyl, is neutral. The acid amides thus formed are called *amic acids*. Glycollic acid, for example, yields glycollamic acid and glycollamide, both containing $C_2H_5NO_2$:

CH_2OH	CH_2NH_2	CH_2OH
$COOH$	$COOH$	$CONH_2$
Glycollic acid.	Glycollamic acid.	Glycollamide.

These amic acids and amides are sometimes represented as derived from a molecule of ammonia and a molecule of water, bound together by the substitution of a diatomic acid-radical for two atoms of hydrogen; thus:

$\left.\begin{matrix}H_3\\H_2\end{matrix}\right\}N$	$\left.\begin{matrix}H_2\\(C_2H_2O)''\\H\end{matrix}\right\}N$
	O
Type.	Glycollamic acid.

The amic acids of this group are identical with the amidated acids derived from the corresponding monatomic acids, $C_nH_{2n}O_2$, by substitution of amidogen for hydrogen; thus glycollamic acid is identical with amidacetic acid; lactamic with amidopropionic; leucamic with amidocaproic acid; for example:

CH_3	$CH_2(NH_2)$	$CH_2(OH)$
$COOH$	$COOH$	$COOH$
Acetic acid.	Amidacetic or Glycollamic acid.	Glycollic acid.

These amic acids are formed, as already observed, by the action of ammonia on the monochlorinated or monobrominated derivatives of the fatty acids; the corresponding neutral amides are produced by the action of ammonia, in the gaseous state or in alcoholic solution, on the corresponding oxides or anhydrides, or on the ethylic ethers of glycollic and lactic acids; thus:

$$\underset{\text{Lactide.}}{C_3H_4O_2} + NH_3 = \underset{\text{Lactamide.}}{C_3H_7NO_2}$$

$$\underset{\text{Ethyl lactate.}}{\begin{matrix}C_2H_4(OH)\\|\\CO(OC_2H_5)\end{matrix}} + NH_2H = \underset{\text{Alcohol.}}{HOC_2H_5} + \underset{\text{Lactamide.}}{\begin{matrix}C_2H_4OH\\|\\CONH_2\end{matrix}}$$

Leucamide, the neutral ether of leucic acid, is not known.

The amic acids of this series possess basic as well as acid properties, and are therefore often designated by names ending in *ine*, the ordinary ter-

mination for organic bases, glygollamic acid being designated as glycocine, lactamic acid as alanine, leucamic acid as leucine (pp. 614, 615, 620).

Amidobenzoic acid, $C_7H_5(NH_2)O_2$, or $C_6H_4(NH_2).CO_2H$, produced from nitro-benzoic acid, $C_7H_4(NO_2)O_2$, by the action of hydrogen sulphide, may also be regarded as *oxy-benzamic acid*, derived from oxy-benzoic acid, $C_6H_4(OH).CO_2H$, by substitution of NH_2 for OH.

Diamidobenzoic acid, $C_7H_4(NH_2)_2O_2$, formed in like manner from dinitrobenzoic acid, may also be viewed as *dioxybenzamic acid*, derived from a hypothetical dioxybenzoic acid, $C_6H_3(OH)_2.CO_2H$; but according to the mode of formation of these acids, they are more conveniently regarded as derivatives of benzoic acid. Similar remarks apply to the amidated acids derived from the homologues of benzoic acid.

AMIDES DERIVED FROM DIATOMIC AND BIBASIC ACIDS.

Each acid of this group may give rise to three amides: viz., 1. An *acid, amide*, or *amic acid*, formed from the acid ammonium-salt by abstraction of one molecule of water. — 2. A neutral *monamide* or *imide*, formed from the acid ammonium-salt by abstraction of two molecules of water. — 3. A neutral *diamide*, derived from the neutral ammonium-salt by abstraction of two molecules of water. Thus from succinic acid, $(C_4H_4O_2)''(OH)_2$ are derived:

$$\underset{\text{Acid ammonium succinate.}}{C_4H_5(NH_4)O_4} - H_2O = \underset{\text{Succinamic acid.}}{C_4H_7NO_3} = (C_4H_4O_2)''(NH_2)(OH) = \left.\begin{matrix}(C_4H_4O_2)''\\ H\end{matrix}\right\}O\,N \qquad \left.\begin{matrix}H_2\end{matrix}\right.$$

$$\underset{\text{Acid salt.}}{C_4H_5(NH_4)O_4} - 2H_2O = \underset{\text{Succinimide.}}{C_4H_5NO_2} = (C_4H_4O_2)''(NH)'' = \left.\begin{matrix}(C_4H_4O_2)''\\ H\end{matrix}\right\}N$$

$$\underset{\text{Neutral salt.}}{C_4H_4(NH_4)_2O_4} - 2H_2O = \underset{\text{Succinamide.}}{C_4H_8N_2O_2} = (C_4H_4O_2)''(NH_2)_2 = \left.\begin{matrix}(C_4H_4O_2)''\\ H_4\end{matrix}\right\}N_2$$

The amic acids of this group are produced:

1. By the action of heat on the acid ammonium-salts of the corresponding acids.

2. By the action of aqueous ammonia on the neutral ethers of bibasic acids; *e. g.*:

$$\underset{\text{Ethyl oxalate.}}{(C_2O_2)''(OC_2H_5)_2} + NH_3 + H(OH) = \underset{\text{Alcohol.}}{2H(OC_2H_5)} + \underset{\text{Oxamic acid.}}{(C_2O_2)''(NH_2)(OH)}$$

3. By boiling imides with ammonia, under which circumstances they take up a molecule of water and are converted into amic acids; thus succinimide, $C_4H_5NO_2$, with H_2O forms succinamic acid, $C_4H_7NO_3$.

The typic or extra-radical hydrogen in these amides may also be replaced by alcoholic or by acid radicals, thereby producing alkalamides, secondary and tertiary diamides, &c. The mode of producing such compounds may be understood from the following equations:

$$\underset{\text{Acid methylammonium oxalate.}}{(C_2O_2)''(ONH_3CH_3)OH} - H_2O = \underset{\text{Methyloxamic acid.}}{(C_2O_2)''NH(CH_3).(OH)}$$

$$\underset{\text{Succinic oxide.}}{(C_4H_4O_2)''O} + NH_2(C_6H_5) = 2H_2O + \underset{\text{Phenylsuccinimide.}}{N(C_6H_5)(C_4H_4O_3)''}$$
(Aniline.)

$$\underset{\text{Ethyl oxalate.}}{(C_2O_2)''(OC_2H_5)_2} + 2NH_2(CH_3) = \underset{\text{Ethyl alcohol.}}{2H(OC_2H_5)} + \underset{\text{Dimethyl-oxamide.}}{N_2H_2(C_2O_2)''(CH_3)_2}$$
(Methylamine.)

$(CO)Cl_2$ + $2NH_2(C_6H_5)$ = $2HCl$ + $N_2H_2(CO)''(C_6H_5)_2$
Carbonyl chloride. Aniline. Diphenyl-carbonide.

$2N(C_4H_4O_2)''Ag$ + $(C_4H_4O_2)''Cl_2$ = $2AgCl$ + $N_2(C_4H_4O_2)''_3$
Argentosuccinimide. Succinyl chloride. Trisuccinamide.

Amides of Carbamic Acid. — *Carbonic acid*, $(CO)''(NH_2)(OH)$, is not known in the free state, that is, as a hydrogen-salt, but its ammonium-salt, $(CO)''(NH_2)(ONH_4)$, is produced, as already noticed (p. 314), by the direct combination of carbon dioxide and ammonia-gas. This salt is easily obtained pure and in large quantity by passing the two gases, both perfectly dry, into cold absolute alcohol, separating the copious crystalline precipitate by filtration from the greater part of the liquid, and heating it with absolute alcohol in a sealed tube to 100°, or above.* The liquid, on cooling, deposits ammonium carbamate in large crystalline laminæ. This salt, if perfectly dried over oil of vitriol, and then heated in a sealed tube to 130°–140° C. (266°–284° F.), splits up into ammonium carbonate and urea, one molecule of it giving up a molecule of water to another:

$2CN_2H_6O_2$ = CN_2H_4O + $CN_2H_8O_3$
Ammonium carbamate. Urea. Ammonium carbonate.

Hence Kolbe concludes that urea is the amide of carbamic acid, not the amide of carbonic acid; but it is not easy to see in what the supposed difference consists; for carbonic acid being $(CO)''(OH)(OH)$, and carbamic acid, $(CO)''(NH_2)(OH)$, the amide of the latter must be identical with the diamide of the former. It appears, also, from the observations of Basaroff, that ordinary commercial ammonium carbonate, when treated in the manner just described, likewise yields urea. On the other hand, the experiments of Wanklyn and Gamgee, already quoted (p. 722), seem to show that urea is essentially different from carbamide.†

Carbamic Ethers. — Carbamic acid forms acid and neutral ethers, accordingly as an atom of hydrogen in the group NH_2 or OH is replaced by an alcohol-radical.

Ethylcarbamic acid, $(CO)''.NH(C_2H_5).OH$, is not known in the free state, but its ethylammonium-salt, $(CO)''.NH(C_2H_5).ONH_3(C_2H_5)$, is produced, as a snow-white powder, by passing carbon dioxide into anhydrous ethylamine cooled by a freezing mixture. Its aqueous solution, like that of ammonium carbamate, does not precipitate barium chloride unless aided by heat. The methylammonium-salt of *methylcarbamic acid* is obtained in a similar manner. *Phenylcarbamic acid*, $(CO)''.NH(C_6H_5).OH$, also called *carbanilic* and *anthranilic acid*, isomeric with amidobenzoic acid, is obtained by boiling indigo with potash and manganese dioxide. It is a crystalline body, soluble in water, and converted by nitrous acid into salicylic (phenyl-carbonic) acid, with evolution of nitrogen:

$(CO)''.NH(C_6H_5).OH + NO_2H = (CO)''.OC_6H_5.OH + H_2O + N_2$.
Phenyl-carbamic acid. Phenyl-carbonic acid.

The neutral carbamic ethers are called *urethanes*. *Ethyl carbamate*, $(CO)''.NH_2.OC_2H_5$, called simply *urethane*, is formed by leaving ethyl car-

* *Kolbe* and *Basaroff*, Chem. Soc. Journal [2], vi. 194.

† Basaroff's experiments have not yet been published in detail, and there is no proof given in the paper above referred to, that the compound obtained by the dehydration of ammonium carbamate was really urea and not carbamide.

bonate in contact with aqueous ammonia; and by the action of ammonia on ethyl chlorocarbonate (alcohol saturated with carbonyl chloride):

$$(CO)''(OC_2H_5)Cl + NH_3 = HCl + (CO)''(NH_2)(OC_2H_5)$$

It forms colorless crystals easily soluble in water. *Methyl carbamate, methylic urethane* or *urethylane,* and *amyl carbamate* or *amylic urethane,* are obtained in like manner.

Carbamic acid in which the whole of the oxygen is replaced by sulphur, constitutes *sulpho-carbamic acid,* $(CS)''(NH_2)(SH)$. There is also an *oxysulpho-carbamic acid,* $(CS)''(NH_2)(OH)$, the ethylic ether of which is *xanthamide,* $(CS)''(NH_2)(OC_2H_5)$ (p. 651).

Carbimide, $(CO)''(NH)''$ or $N\left\{\begin{matrix}(CO)''\\H\end{matrix}\right.$, is the same as cyanic acid; and many of the reactions of cyanic acid are most naturally represented by the formula just given, especially its conversion into carbon dioxide and ammonia under the influence of acids or alkalies:

$$NH(CO)'' + H_2O = NH_3 + (CO)''O,$$

and the corresponding formation of ethylamine and its homologues by distilling cyanic ethers with potash.

Carbamide, CN_2H_4O or $N_2(CO)''H_4$. — This compound is produced by the action of ammonia-gas on carbonyl chloride:

$$COCl_2 + 2NH_3 = 2HCl + N_2COH_4;$$

also by the action of ammonia on ethyl carbonate, and by the decomposition of oxamide at a red heat: $C_2O_2N_2H_4 = CON_2H_4 + CO$. It bears a very close resemblance to urea; the only difference indeed yet observed between the two compounds, is in the products which they yield when oxidized by potassium permanganate in presence of free alkali (p. 722).

Amides of Oxalic Acid. — *Oxamic acid,* $C_2NH_3O_3 = (C_2O_2)''(NH_2)(OH)$, is produced by heating acid ammonium oxalate to about 230°; also as an ammonium-salt by boiling oxamide with aqueous ammonia: $C_2H_4N_2O_2 + H_2O = C_2H_2(NH_4)NO_3$. Oxamic acid is a white crystalline powder, sparingly soluble in cold water, still less soluble in alcohol and ether. It is monobasic, and forms numerous crystalline metallic salts.

Oxamic ethers may be formed by substitution of ethyl-radicals for hydrogen, either in the group NH_2 or in the group OH of oxamic acid, the resulting ethers being acid in the former case, neutral in the latter. The neutral ethers, also called *oxamethanes* (p. 660), are formed by the action of ammonia, in the gaseous state or in alcoholic solution, on neutral oxalic ethers; thus:

$$\underset{\text{Ethyl oxalate.}}{(C_2O_2)''(OC_2H_5)_2} + NH_3 = \underset{\text{Alcohol.}}{HOC_2H_5} + \underset{\text{Ethyl oxamate.}}{(C_2O_2)''(NH_2)(OC_2H_5)}$$

They are crystalline bodies soluble in alcohol, decomposed by boiling water, yielding ammonium oxalate and the corresponding alcohol.

The acid ethers of oxamic acid, containing one equivalent of alcohol-radical, are produced by dehydration of the acid oxalates of the corresponding amines; thus:

$$\underset{\substack{\text{Acid ethylammonium}\\\text{oxalate.}}}{(C_2O_2)''(ONH_3C_2H_5)(OH)} - OH_2 = \underset{\text{Ethyloxamic acid.}}{(C_2O_2)''[NH(C_2H_5)](OH)}$$

Methyloxamic and phenyloxamic acids are also known. These acid ethers are metameric with the neutral oxamic ethers containing the same alcohol-radicals.

The replacement of both the hydrogen-atoms in the group NH_2 in oxamic acid, would also yield monobasic acid ethers; none of these are, however, known in the free state, but the ethylic ethers of dimethyl- and diethyl-oxamic acids have been obtained; *e. g.*, *ethylic dimethyl-oxamate*, $(C_2O_2)''N(CH_3)_2(OC_2H_5)$.

The *imide* of oxalic acid is not known.

Oxamide, $N_2(C_2O_2)''H_4$. — This compound is produced by the action of heat on neutral ammonium oxalate (p. 659), but is more advantageously prepared by the action of ammonia on neutral ethyl oxalate. It is also formed in several reactions from cyanogen and cyanides: an aqueous solution of hydrocyanic acid, mixed with hydrogen dioxide, yields a crystalline deposit of oxamide: $2CNH + H_2O_2 = C_2N_2H_4O_2$.

Oxamide is a white, light, tasteless powder, insoluble in cold water, slightly soluble in boiling water, insoluble in alcohol. Heated in an open tube, it volatilizes and forms a crystalline sublimate; but its vapor, passed through a red-hot tube, is completely resolved into carbon monoxide, ammonium carbonate, hydrocyanic acid, and urea (or carbamide):

$$2C_2N_2H_4O_2 = CO + CO_2 + NH_3 + CNH + CN_2H_4O.$$

Dilute mineral acids decompose it, yielding an ammonium-salt and free oxalic acid; *e. g.:*

$$C_2N_2H_4O_2 + SO_4H_2 + 2H_2O = SO_4(NH_4)_2 + C_2H_2O_4.$$

Dimethyloxamide, $N_2(C_2O_2)''H_2(CH_3)_2$, is produced by the dry distillation of methylammonium oxalate:

$$C_2(CH_6N)_2O_4 - 2H_2O = C_2N_2H_2(CH_3)_2O_2.$$

Diethyloxamide, diamyloxamide, diphenyloxamide, and dinaphthyloxamide, are obtained in a similar manner.

AMIDES DERIVED FROM ACIDS OF HIGHER ATOMICITY.

Our knowledge of these amides is somewhat limited: we shall notice only those derived from malic and from citric acid.

Malic acid, $(C_4H_3O_2)'''(OH)_3$, which is triatomic and bibasic, forms an acid amide and a neutral amide:

$(C_4H_3O_2)'''\{OH, OH, OH$	$(C_4H_3O_2)'''\{OH, NH_2, OH$	$(C_4H_3O_2)'''\{OH, NH_2, NH_2$
Malic acid.	Malamic acid.	Malamide.

Malamide is deposited in small crystals, when ammonia-gas is passed into an alcoholic solution of ethyl malate:

$C_4H_4(C_2H_5)_2O_5$	+	$2NH_3$	=	$2C_2H_6O$	+	$C_4H_8N_2O_3$
Ethyl malate.				Alcohol.		Malamide.

Malamic acid, $C_4H_7NO_4$, is not known in the free state; but its ethylic

ether, or *malamethane*, $C_4H_6(C_2H_5)NO_4$, is produced as a crystalline mass, when dry ethyl malate is saturated with ammonia-gas:

$$C_4H_4(C_2H_5)_2O_5 + NH_3 = C_2H_6O + C_4H_6(C_2H_5)NO_4.$$

Malamide is metameric, not identical, with *asparagin*, a substance found in the root of marsh-mallow, in asparagus-shoots, and in several other plants. To prepare asparagin, marsh-mallow roots are chopped small, and macerated in the cold with milk of lime; the filtered liquid is precipitated by carbonate of ammonia; and the clear solution evaporated in the water-bath to a syrupy state. The impure asparagin, which separates after a few days, is purified by re-crystallization. Asparagin forms brilliant, transparent, colorless crystals, which have a faint, cooling taste, and are freely soluble in water, especially when hot. When dissolved in a saccharine liquid, which is afterward made to ferment, or when heated with water under pressure in a close vessel, or when boiled with an acid or an alkali, it is converted into ammonia and *aspartic acid*, an acid metameric with malamic acid.

Asparagin differs from malamide in crystalline forms; moreover, it contains water of crystallization, the composition of the crystals being $C_4H_8N_2O_3 . H_2O$, whereas those of malamide are anhydrous. The two substances differ also in their action on polarized light, malamide having a specific rotatory power of —47·5°, whereas that of asparagin in an acid solution is + 35°, and in an ammoniacal solution —11° 18′. Lastly, malamide, when treated with alkalies, is easily resolved into ammonia and malic acid, whereas asparagin, as already observed, yields ammonia and aspartic acid.

The difference of constitution between these metameric bodies may be represented by the following formulæ:

COOH	COOH	$CONH_2$	$CONH_2$	$CONH_2$
|	|	|	|	|
CHOH	$CHNH_2$	CHOH	$CHNH_2$	CHOH
|	|	|	|	|
CH_2	CH_2	CH_2	CH_2	CH_2
|	|	|	|	|
COOH	COOH	COOH	COOH	$CONH_2$
Malic acid.	Aspartic acid.	Malamic acid.	Asparagin.	Malamide.

These formulæ indicate that aspartic acid is bibasic, malamic acid and asparagin monobasic, and malamide neutral. Now, malamide is certainly neutral, and asparagin forms salts by substitution of metals for *one* of its hydrogen-atoms. The basicity of malamic and aspartic acids is not very distinctly made out. Aspartic acid is commonly said to be monobasic, forming neutral salts, like $C_4H_6KNO_4$, and likewise basic salts; but the aspatates have not been very fully investigated, and it is quite possible that these so-called basic salts may really be neutral.

There are also phenylated amides of malic acid, viz., *diphenyl-malamide* or *malanilide*, $C_4H_6(C_6H_5)_2N_2O_3$, and *phenyl-malimide* or *malanil*, $C_{10}H_9NO_3 = (C_4H_3O_2)'''\begin{cases}(NH)''\\OC_6H_5\end{cases}$, produced simultaneously by fusing malic acid with aniline; and *phenyl-malamic* or *malanilic acid*, $C_{10}H_{11}NO_4 = (C_4H_3O_2)'''\begin{cases}OC_6H_5\\NH_2\\OH\end{cases}$, obtained as an ammonium-salt by boiling phenyl-malimide with aqueous ammonia.

Lastly, the action of heat on acid ammonium-malate yields *malamyl-nitrile*, $(C_4H_3O_2)'''N$, which is identical with the imide of fumaric acid, and when

boiled with hydrochloric or nitric acid, yields compounds of these acids with an optically inactive variety of aspartic acid: $C_4H_3O_2N + 2H_2O = C_4H_7NO_4$.

Amides of Citric Acid. — *Citramide*, $N_3(C_6H_5O_4)'''H_6$, is a crystalline compound, slightly soluble in water, obtained by the action of alcoholic ammonia on ethyl or methyl citrate. — *Triphenyl-citramide*, $N_3(C_6H_5O_4)'''(C_6H_5)_3H_3$, obtained by the action of heat on neutral phenylammonium citrate, $C_6H_5(C_6H_8N)_3O_4$, from which it differs by $3H_2O$, crystallizes from alcohol in colorless striated prisms.

Citrimide and citramic acid are not known; but phenylic derivatives of these amides have been obtained.

UNCLASSIFIED ORGANIC COMPOUNDS.

There are still many organic compounds, especially those obtained from natural sources, which cannot, in the present state of our knowledge, be included with certainty in either of the preceding groups or series. Some of these have been described in connection with the more definitely known compounds to which they are most closely allied in their origin or properties. It remains to describe the Organic Coloring principles, the Resins and Balsams, and the Albuminous and Gelatinous principles of the living organism; these last, however, will be most conveniently described under the head of "Animal Chemistry."

ORGANIC COLORING PRINCIPLES.

The organic coloring principles are substances of very considerable practical importance in relation to the arts; several of them, too, have been made the subjects of extensive and successful chemical investigation. With the exception of one red dye, cochineal, they are all of vegetable origin.

The art of dyeing is founded upon an affinity or attraction existing between the coloring matter of the dye and the fibre of the fabric. In wool and silk this affinity is usually very considerable, and to such tissues a permanent stain is very easily communicated; but with cotton and flax it is much weaker. Recourse is then had to a third substance, which does possess such affinity in a high degree, and with this the cloth is impregnated. Such substances are termed *mordants*. Alumina, ferric oxide, and stannic oxide are bodies of this class.

When an infusion of some dye-wood, as logwood, for example, is mixed with alum and a little alkali, a precipitate falls, consisting of alumina in combination with coloring matter, called a *lake;* it is by the formation of this insoluble substance within the fibre that a permanent dyeing of the cloth is effected. Ferric oxide usually gives rise to dull, heavy colors; alumina and stannic oxide, especially the latter, to brilliant ones. It is easy to see that, by applying the mordant *partially* to the cloth, by a wood-block or otherwise, a pattern may be produced, as the color will be removed from the other portions by washing.

Indigo.—Indigo is the most important member of the group of blue coloring matters. It is the product of several species of the genus *Indigofera*, which grow principally in warm climates. When the leaves of these plants are placed in a vessel of water and allowed to ferment, a yellow substance is dissolved out, which by contact of air becomes deep-blue and insoluble, and finally precipitates. This, washed and carefully dried, constitutes the indigo of commerce. It is not contained ready formed in the plant, but is produced by the oxidation of some substance there present. Neither is the fermentation essential, as a mere infusion of the plant in hot water deposits indigo by standing in the air.

The occurrence of small quantities of indigo in urine had been observed by Hassall and others: it was, however, generally considered as a morbid secretion; but lately Dr. Schunck has proved that traces of indigo may be procured from healthy urine. The process by means of which this object

may be obtained is rather complicated. For a description of this process, and for a full account of his researches on the formation of indigo-blue, which would overstep the limits of this elementary work, the reader is referred to Dr. Schunck's original papers.*

Indigo comes into the market in the form of cubic cakes, which, when rubbed with a hard body, exhibits a copper-red appearance: its powder has a deep-blue tint. The best indigo is so light as to float upon water. In addition to the blue coloring matter, or true indigo, it contains at least half its weight of various impurities, among which may be noticed a red resinous matter, the *indigo-red* of Berzelius: these may be extracted by boiling the powdered indigo in dilute acid, in alkali, and afterwards in alcohol.

Pure indigo is quite insoluble in water, alcohol, oils, dilute acids, and alkalies; it dissolves in about 15 parts of concentrated sulphuric acid, forming a deep-blue pasty mass, entirely soluble in water, and often used in dyeing; this is *sulphindylic* or *sulphindigotic acid*, a compound analogous to ethyl-sulphuric acid, capable of forming with alkaline bases blue salts, which, though easily soluble in pure water, are insoluble in saline solutions. If an insufficient quantity of sulphuric acid has been employed, or the digestion not long enough continued, a purple powder is left on diluting the acid mass, soluble in a large quantity of pure water. The Nordhausen acid answers far better for dissolving indigo than ordinary oil of vitriol. Indigo may, by cautious management, be volatilized: it forms a fine purple vapor, which condenses in brilliant copper-colored needles. The best method of subliming this substance is, according to Mr. Taylor, to mix it with plaster of Paris, make the whole into a paste with water, and spread it upon an iron plate. 1 part indigo and 2 parts plaster answer very well. This, when quite dry, is heated by a spirit-lamp: the volatilization of the indigo is aided by the vapor of water disengaged from the gypsum, and the surface of the mass becomes covered with beautiful crystals of pure indigo, which may be easily removed by a thin spatula. At a higher temperature, charring and decomposition take place.

In contact with deoxidizing agents, and with an alkali, indigo suffers a very curious change: it becomes soluble and nearly colorless, perhaps returning to the same state in which it existed in the plant. It is on this principle that the dyer prepares his *indigo-vat:* 5 parts of powdered indigo, 10 parts of green vitriol, 15 parts of slaked lime, and 60 parts of water, are agitated together in a close vessel, and then left to stand. The ferrous hydrate, in conjunction with the excess of lime, reduces the indigo to the soluble state: a yellowish liquid is produced, from which acids precipitate the *white* or *deoxidized* indigo as a flocculent insoluble substance, which absorbs oxygen with the greatest avidity, and becomes blue. Cloth, steeped in the alkaline liquid, and then exposed to the air, acquires a deep and most permanent blue tint by the deposition of solid insoluble indigo in the substance of the fibre. Instead of the iron salt and lime, a mixture of dilute caustic soda and grape-sugar dissolved in alcohol may be used: the sugar becomes oxidized to formic acid, and the indigo reduced. On allowing a solution of this description to remain in contact with the air, it absorbs oxygen, and deposits the indigo in the crystalline state.

The following formulæ represent the composition of the bodies just described:

Blue insoluble indigo	C_8H_5NO.
White, or reduced indigo † . . .	$C_{16}H_{12}N_2O_2$.
Sulphindylic acid	$C_8H_5NO . SO_3$.

* Memoirs of the Literary and Philosophical Society of Manchester, vol. xii. 177; xiv. 181, 239; also Philosophical Magazine [3], x. 73; xv. 99; [4], xv. 29, 117.

† Properly *hydrogenized* indigo, if the above be the correct view; white indigo may, however, be viewed as a *hydrate*, and blue indigo as an oxide of one and the same substance:

White indigo	$C_{16}H_{10}N_2O . H_2O$.
Blue indigo	$C_{16}H_{10}N_2O . O$.

Products of the Decomposition of Indigo. — The products of the destructive modifications of indigo by powerful chemical agents of an oxidizing nature are both numerous and interesting, inasmuch as they connect this substance in a very curious manner with several other groups of organic bodies, especially with those of the salicyl and phenyl series. Many of them are exceedingly beautiful, and possess very remarkable properties.

Isatin, $C_3H_5NO_2$. — To prepare this substance, which contains the elements of indigo with 1 atom of oxygen, 1 part of indigo reduced to fine powder, and rubbed to a paste with water, is gently heated with a mixture of 1 part of sulphuric acid and 1 part of potassium bichromate dissolved in 20 or 30 parts of water. The indigo dissolves, with very slight disengagement of carbon dioxide, towards the end, forming a yellow-brown solution, which, on standing, deposits impure *isatin* in crystals. These are collected, slightly washed, and redissolved in boiling water: the filtered solution on cooling deposits the isatin in a state of purity. Or, powdered indigo may be mixed with water to a thin paste, heated to the boiling point in a large capsule, and nitric acid added by small portions until the blue color disappears: the whole is then largely diluted with boiling water, and filtered. The impure isatin which separates on cooling is washed with water containing a little ammonia, and recrystallized. Both these processes require careful management, or the oxidizing action proceeds too far, and the product is destroyed.

Isatin forms deep yellowish-red prismatic crystals of great beauty and lustre: it is sparingly soluble in cold water, freely in boiling water, and also in alcohol. The solution colors the skin yellow, and causes it to emit a very disagreeable odor. Isatin cannot be sublimed.

A solution of potash dissolves isatin with purple color: from this solution acids precipitate the isatin unchanged. On boiling, however, the color is destroyed, and the liquid yields on evaporation crystals of the potassium-salt of *isatic acid*, $C_8H_7NO_3$. In the free state this is a white and imperfectly crystalline powder, soluble in water, and easily decomposed into isatin and water.

By chlorine isatin is converted into *chlorisatin*, $C_8H_4ClNO_2$, a body closely resembling isatin itself in properties. If an alcoholic solution and excess of chlorine be employed, other products make their appearance, as *chloranil*, $C_6Cl_4O_2$, *trichlorophenol*, $C_6H_3Cl_3O$, and a resinous substance. The former of these substances, the position of which in the quinone series has been already noticed (p. 681), yields further products with potash and ammonia. *Bromisatin* is easily formed. The change which isatin and its chlorinated and brominated congeners undergo when submitted to the action of fusing potassium hydrate has been already considered in the section on the Organic Bases (p. 740).

Exposed to the action of hydrogen and ammonium sulphide, isatin yields several new compounds, as *isathyde*, *sulphisathyde*, &c.

A hot solution of isatin, treated with ammonium sulphide, gives rise to a deposit of sulphur, a white crystallized substance being produced at the same time: it has received the name of *isathyde*, and contains $C_8H_6NO_2$. It bears to isatin the same relation as white to blue indigo. If the ammonium sulphide be replaced by hydrogen sulphide, *bisulphisathyde*, C_8H_6NOS, is produced, which is derived from the former by substitution of one atom of sulphur for oxygen. An alcoholic solution of potash converts this last compound into *sulphisathyde*, $C_{16}H_{12}N_2O_3S$, or a double molecule of isathyde in which one quarter of the oxygen is replaced by sulphur. Under the influence of cold aqueous solution of potash, bisulphisathyde yields *indin*, C_8H_6NO, which is polymeric with white indigo. When treated with boiling

potash, indin fixes the elements of one molecule of water, and becomes *indinic acid*, $C_8H_5NO_2$, the potassium-salt of which forms fine black needles.

Ammoniacal gas and solution of ammonia yield with isatin a series of interesting substances, containing the nitrogen of the ammonia in addition to that of the isatin.

Action of Chlorine on Indigo. — In the dry state chlorine has no action whatever on indigo, even at the temperature of 100°. In contact with water, the blue color is instantly destroyed, and cannot again be restored. The same thing happens with the blue solution of sulphindylic acid. When chlorine is passed into a mixture of powdered indigo and water until the color disappears, and the product is then distilled into a retort, water containing hydrochloric acid and a mixture of two volatile bodies, trichloraniline, $C_6H_4Cl_3N$, and trichlorophenol, $C_6H_3Cl_3O$, pass over into the receiver, while the residue in the retort is found to contain chlorisatin, already mentioned, and *bichlorisatin*, $C_8H_3Cl_2NO_2$, much resembling the former, but more freely soluble in alcohol. Both these bodies yield acids in contact with boiling solution of potash, by assimilating the elements of water.

The action of bromine on indigo is very similar.

Anilic and Picric Acids. — Anilic or indigotic acid is prepared by adding powdered indigo to a boiling mixture of 1 part of nitric acid and 10 parts of water, until the disengagement of gas ceases, filtering the hot dark-colored liquid, and allowing it to stand. The impure anilic acid so obtained is converted into the lead-salt, which is purified by crystallization and the use of animal charcoal, and then decomposed by sulphuric acid. Anilic acid forms fine white or yellowish needles, which have a feebly acid taste, and a very sparing degree of solubility in cold water. In hot water and in alcohol it dissolves easily. It melts when heated, and on cooling assumes a crystalline structure. By careful management it may be sublimed unchanged. Anilic acid contains $C_7H_5NO_5 = C_7H_5(NO_2)O_3$. The same acid is readily prepared from salicylic acid (p. 655). Hence it is more appropriately called *nitrosalicylic acid.*

Picric, carbazotic, or *nitrophenisic acid,* $C_6H_3(NO_2)_3O$, already described among the derivatives of phenol (p. 552), is also one of the ultimate products of the action of nitric acid upon indigo.

Products of the Action of Potassium Hydrate upon Indigo. — One of the most remarkable of these, aniline, has been already described (p. 739). When powdered indigo is boiled with a very concentrated solution of caustic potash, it is gradually dissolved, with the exception of some brownish flocculent matter, and the liquid on cooling deposits yellow crystals of the potassium-salt of *chrysanilic acid,* which can be procured in a purer state by dissolving the crystals in water, filtering from reproduced indigo, and adding a slight excess of mineral acid. Chrysanilic acid can be obtained in indistinct crystals from weak alcohol; it is supposed to contain $C_{28}H_{22}N_4O_6$; but it is very probably a mixture of several substances, especially isatic acid.

When this substance is boiled with mineral acids, it is decomposed into *anthranilic,* or *phenyl-carbamic acid,* $C_7H_7NO_2$ (p. 776), which remains in solution, and a blue insoluble matter resembling indigo: a similar effect is slowly produced by the action of the air upon an alcoholic solution of chrysanilic acid. Anthranilic acid is colorless, sparingly soluble in cold water, easily soluble in alcohol. It melts when heated, sublimes under favorable circumstances, but decomposes entirely when heated in a narrow tube into carbon dioxide and aniline. By treatment with nitrous acid, it is converted into salicylic acid.

According to Cahours, pure indigo can also be converted into salicylic

acid by fusion with potash: a particular temperature is required, somewhat above 299° C. (570° F.), and the operation is by no means always successful.

Lichens. — *Litmus* is used by the dyer as a red coloring matter; the chemist employs it in the blue state as a test for the presence of acid, by which it is instantly reddened.

In preparing test-papers for chemical use with infusion of litmus, good writing or drawing paper, free from alum and other acid salts, should be chosen. Those sheets which after drying exhibit red spots, or patches, may be reddened completely by a little dilute acetic acid, and used, with much greater advantage than tumeric-paper, to discover the presence of free alkali, which restores the blue color.

Many liquids, when exposed in a moistened state to the action of ammonia, yield purple or blue coloring principles, which, like indigo, do not pre-exist in the plant itself. Thus, the *Roccella tinctoria*, the *Variolaria orcina*, the *Lecanora tartarea*, &c., when ground to paste with water, mixed with putrid urine or solution of ammonium carbonate, and left for some time freely exposed to the air, furnish the *archil*, *litmus*, and *cudbear* of commerce, very similar substances, differing chiefly in the details of the preparation. From these the coloring matter is easily extracted by water or very dilute solution of ammonia.

The lichens have been extensively examined by Schunck, Stenhouse, and several other chemists. The whole subject has been lately revised by Strecker, whose formulæ have been adopted in the following succinct account:

Erythric Acid. — The lichen *Roccella tinctoria*, from which the finest kind of archil is prepared, is boiled with milk of lime; the filtered solution is precipitated by hydrochloric acid, and the precipitate dried and dissolved in warm, not boiling alcohol, from which on cooling crystals of erythric acid are deposited. This is a very feeble acid, colorless, inodorous, difficultly soluble in cold and even in boiling water, readily soluble in ether. Its solution, when mixed with chloride of lime, assumes a blood-red color. Boiled with water for some time, erythric acid absorbs one molecule and yields *picro-erythrin*, a crystallizable, bitter principle, and *orsellinic acid*. If the ebullition be continued, the orsellinic acid undergoes a further change, being converted into *orcin* (p. 552).

Picro-erythrin, boiled with baryta-water, is decomposed into orcin, erythrite (p. 571), and carbon dioxide.

The composition of these various substances is expressed by the following formulæ:

Erythric acid	$C_{20}H_{22}O_{10}$.
Orsellinic acid	$C_8H_8O_4$.
Picro-erythrin	$C_{12}H_{16}O_7$.
Orcin	$C_7H_8O_2$.

And the successive changes which occur by ebullition are represented by the following equations:

$$\underset{\text{Erythric acid.}}{C_{20}H_{22}O_{10}} + H_2O = \underset{\text{Orsellinic acid.}}{C_8H_8O_4} + \underset{\text{Picro-erythrin.}}{C_{12}H_{16}O_7}.$$

$$\underset{\text{Orsellinic acid.}}{C_8H_8O_4} = \underset{\text{Orcin.}}{C_7H_8O_2} + CO_2.$$

$$\underset{\text{Picro-erythrin.}}{C_{12}H_{16}O_7} + H_2O = \underset{\text{Orcin.}}{C_7H_8O_2} + \underset{\text{Erythro-mannite.}}{C_4H_{10}O_4} + CO_2.$$

Lecanoric or Alpha-orsellic Acid is obtained from the South American variety of *Roccella tinctoria*. The preparation and the properties of this substance are perfectly analogous to those of erythric acid. It contains $C_{16}H_{14}O_7$, and likewise yields orsellinic acid by boiling with baryta-water:

$$\underset{\text{Lecanoric acid.}}{C_{16}H_{14}O_7} + H_2O = \underset{\text{Orsellinic acid.}}{2C_8H_8O_4}$$

If the ebullition be too long continued, a great portion of the orsellinic acid is converted into orcin.

Orsellinic Acid, whether prepared from erythric or lecanoric acid, forms crystals which are far more soluble in water than either of the acids from which it has been prepared. Its taste is somewhat bitter. Boiled with water it yields orcin; under the influence of air and ammonia, it assumes a beautiful purple color.

If the lichens, instead of being treated with milk of lime, are exhausted with boiling alcohol, the erythric and lecanoric acids are likewise decomposed; but instead of orsellinic acid, the ether of this substance, $C_8H_7(C_2H_5)O_4$, is formed. This ether was formerly described under the name *pseudo-erythrin*, until Dr. Schunck pointed out its true nature. Ethyl orsellinate may be likewise produced by boiling pure orsellinic acid with alcohol. It crystallizes in colorless lustrous plates, which are readily soluble in boiling water, alcohol, and ether.

Beta-orsellic Acid is found in *Roccella tinctoria* grown at the Cape: it is obtained like erythric and alpha-orsellic acid, which it resembles in properties. Beta-orsellic acid contains $C_{34}H_{32}O_{15}$: by boiling with water it likewise yields orsellinic acid, together with hair-like crystals of a silvery lustre, of a substance called *roccellinin*, which has the composition $C_{18}H_{16}O_7$.

$$\underset{\text{Beta-orsellic acid.}}{C_{34}H_{32}O_{15}} = \underset{\text{Orsellinic acid.}}{2C_8H_8O_4} + \underset{\text{Roccellinin.}}{C_{18}H_{16}O_7}$$

The decomposition of beta-orsellic acid is obviously analogous to that of erythric acid, the roccellinin representing the picro-erythrin.

Evernic Acid is extracted by milk of lime from *Evernia prunastri*, which was formerly believed to contain lecanoric acid. Evernic acid is very difficultly soluble even in boiling water: it assumes a yellow color with chloride of lime. When boiled with an alkali, it yields another crystalline acid, *everninic acid*, differing from the preceding by its free solubility in boiling water. The composition of evernic acid is represented by the formula $C_{17}H_{16}O_7$, that of everninic acid by $C_9H_{10}O_4$. Evernic acid, when boiled for a considerable time with baryta, yields orcin: everninic acid does not give a trace of this substance. It is therefore probable that evernic acid, under the influence of alkalies, yields, in addition to everninic acid, likewise orsellinic acid, from which the orcin is derived, and that this decomposition is represented by the equation:

$$\underset{\text{Evernic acid.}}{C_{17}H_{16}O_7} + H_2O = \underset{\text{Orsellinic acid.}}{C_8H_8O_4} + \underset{\text{Everninic acid.}}{C_9H_{10}O_4}$$

Parellic Acid. — *Lecanora parella* contains an acid probably analogous to erythric, alpha-orsellic, beta-orsellic, and evernic acids, the composition of which is, however, still unknown. By boiling with baryta it yields orsellinic acid and *parellic acid*, $C_9H_6O_4$.

Orcin, $C_7H_8O_2$, is the general product of decomposition of the acids previously described, under the influence of heat or alkaline earths. It is a diatomic phenol, and has already been described under that head (p. 562).

In contact with ammonia and oxygen it is converted into a deep-red coloring matter called *orcein*, $C_7H_7NO_3$.

Other substances are occasionally present in lichens: thus, the *Usnea barbata* and several other lichens contain *usnic acid*, a substance crystallizing from alcohol in fine yellowish-white needles with metallic lustre, having the formula $C_{19}H_{18}O_7$. It gives no orcin by distillation, but a substance similar to it, which probably contains $C_8H_{10}O_2$, and has been designated by the name of *beta-orcin*. The *Parmelia parietina* furnishes another new substance, *chrysophanic acid*, crystallizing in fine golden-yellow scales, and containing $C_{16}H_8O_3$. It is a very stable substance, and may be sublimed without much decomposition. The same body is present in rhubarb, together with *emodin*, a principle closely resembling chrysophanic acid.

Cochineal. — This is a little insect, the *Coccus cacti*, which lives on several species of *cactus*, found in warm climates, and cultivated for the purpose, as in Central America. The dried body of the insect yields to water and alcohol a magnificent red coloring matter, precipitable by alumina and oxide of tin: *carmine* is a preparation of this kind. In cochineal the coloring matter is associated with several inorganic salts, especially phosphates and nitrogenous substances. Mr. Warren De La Rue, who has published a very elaborate investigation of cochineal,* has separated the pure coloring matter, which he calls *carminic acid*, by the following process: The aqueous decoction of the insect is precipitated by lead acetate, and the impure lead carminate washed and decomposed by hydrogen sulphide: the coloring matter thus separated is submitted again to the same treatment. A solution of carminic acid is thus obtained, which is evaporated to dryness, redissolved in absolute alcohol, and digested with crude lead carbonate, whereby a small quantity of phosphoric acid is separated, and, lastly, mixed with ether, which separates a trace of a nitrogenous substance. The residue now obtained on evaporation is pure carminic acid. It is a purple-brown mass, yielding a fine red powder, soluble in water and alcohol in all proportions, slightly soluble in ether. It is soluble without decomposition in concentrated sulphuric acid, but readily attacked by chlorine, bromine, and iodine, which change its color to yellow. It resists a temperature of 136° C. (277° F.), but is charred when heated more strongly. Carminic acid is a feeble acid. The composition of the substance, dried at 120° C. (248° F.), is represented by $C_{14}H_{14}O_8$, which formula is corroborated by the analysis of a copper compound, $2C_{14}H_{14}O_8 . CuO$.

By the action of nitric acid upon carminic acid, there is formed, together with oxalic acid, a splendid nitrogenetted acid, crystallizing in yellow rhombic plates. This substance, to which the name *nitrococcusic acid* was given, is bibasic: it contains $C_8H_5N_3O_9$. It is soluble in cold, more so in boiling water, and readily soluble in alcohol and ether. Nitrococcusic acid is evidently derived from a non-nitrogenous compound in which part of the hydrogen is replaced by NO_2. Like all substances of this class, it explodes when heated.

In the mother-liquor, from which the carminic acid has been separated, De La Rue discovered a white, crystalline, nitrogenous substance, for which he established the formula $C_9H_{11}NO_3$. This substance is identical with *tyrosine*, which will be mentioned in the section on Animal Chemistry.

Madder. — The root of the *Rubia tinctorum*, cultivated in southern France, the Levant, &c., is the most permanent and valuable of the red dye-stuffs. In addition to several yellow coloring matters, which are of little importance for the purposes of the dyer, madder contains two red pigments, which are called *alizarin* and *purpurin*. These substances have been the

* Memoirs of the Chemical Society, vol. iii. p. 454.

subject of very extensive researches by Debus, Higgins, and especially Schunck. The latest papers on madder have been published by Wolff and Strecker, whose formulæ are quoted in the following abstract:

Alizarin.—The aqueous decoction of madder is precipitated by sulphuric acid, and the precipitate washed and boiled with aluminium chloride, which dissolves the red pigments, an insoluble brownish residue remaining behind. The solution, when mixed with hydrochloric acid, yields a precipitate consisting chiefly of alizarin — still, however, contaminated with purpurin. The impure alizarin thus obtained may be further purified by again throwing down the alcoholic solution with aluminium hydrate, and boiling the precipitate with a concentrated solution of soda, which leaves a pure compound of alumina and alizarin behind. From this the alizarin is separated by hydrochloric acid and recrystallized from alcohol. Pure alizarin crystallizes in splendid red prisms, which may be sublimed. It is but slightly soluble in water and in alcohol, but dissolves in concentrated sulphuric acid with a deep red color. On addition of water, the coloring matter is reprecipitated unchanged. It is also soluble in alkaline liquids, to which it imparts a magnificent purple color. It is insoluble in cold solution of alum. Alizarin is the chief coloring matter of madder: it contains $C_{10}H_6O_3 . 2H_2O$,* and is a feeble acid: a few definite compounds with mineral oxides have been prepared, among which a lime compound, $4C_{10}H_6O_3 . 3CaH_2O_2$, may be mentioned. The action of nitric acid upon alizarin gives rise to the formation of oxalic acid and phthalic acid (p. 666):

$$\underset{\text{Alizarin.}}{C_{10}H_6O_3} + H_2O + O_4 = C_2H_2O_4 + \underset{\text{Phthalic acid.}}{C_8H_6O_4}$$

Purpurin. — Madder is allowed to ferment and then boiled with a strong solution of alum. The solution, when mixed with sulphuric acid, yields a red precipitate, which is purified by re-crystallization from alcohol. Purpurin thus obtained crystallizes in red needles, which contain $C_9H_6O_3 . H_2O$, *i. e.*, one atom of carbon less than alizarin. When treated with nitric acid, purpurin, like alizarin, furnishes oxalic and phthalic acids. Purpurin likewise contributes to the tinctorial properties of madder, but less so than alizarin. Together with alizarin and purpurin, several other substances occur in madder, among which may be noticed an orange pigment, *rubiacin*, convertible by oxidizing agents into a peculiar acid, *rubiacic acid*, a yellow pigment, *xanthin*, a bitter principle, *rabian*, sugar, pectic acid, and several resins, &c.

Garancin is a coloring material, which is produced by the action of sulphuric acid upon madder. This substance possesses a higher tinctorial power than madder itself.

The beautiful *Turkey-red* of cotton cloth is a madder color; it is given by a very complicated process, the theory of which is not yet perfectly elucidated.

Safflower. — This substance contains a yellow and a red coloring matter, the latter being insoluble in water, but soluble in alkaline liquids. The safflower may be exhausted with water acidulated with acetic acid, and the solution mixed with lead acetate, and filtered from the dark-colored impure precipitate. The lead compound of the yellow pigment may then be thrown down by addition of ammonia and decomposed by sulphuric acid. In its purest form the yellow matter constitutes a deep yellow, uncrystallizable, and very soluble substance, very prone to oxidation. In its lead-compound it has probably the composition $C_{24}H_{24}O_{13}$.

The red matter, or *carthamin*, is obtained from the residual safflower by a dilute solution of sodium carbonate; pieces of cotton-wool are immersed

* According to Schunck, the formula of alizarin is $C_{14}H_{10}O_4$.

in the liquid, and acetic acid gradually added. The dried cotton is then digested in a fresh quantity of the alkaline solution, and the liquid supersaturated with citric acid, which throws down the carthamin in carmine-red flocks. It forms, when pure and dry, an amorphous, brilliant, green powder, nearly insoluble in water, but soluble in alcohol with splendid purple color. It contains $C_{14}H_{16}O_7$.

Brazil-wood and *Logwood* give red and purple infusions, which are largely used in dyeing: the coloring principle of logwood is termed *hematoxylin*, and has been obtained in crystals. This substance contains $C_{16}H_{14}O_6$. Acids brighten these colors, and alkalies render them purple or blue.

Among yellow dyes, *quercitron bark*, *fustic-wood*, and *saffron* may be mentioned, and also *turmeric:* these all give yellow infusions to water, and furnish more or less permanent colors.

Purree or Indian yellow, a body of unknown origin, used in water-color painting, is, according to the researches of Stenhouse and Erdmann, a compound of magnesia with a substance termed *purreic* or *euxanthic* acid. The latter, when pure, crystallizes in nearly colorless needles, sparingly soluble in cold water, and of sweetish-bitter taste. It forms yellow compounds with the alkalies and earths, and is decomposed by heat, with production of a neutral crystalline sublimate, *purrenone* or *euxanthone*. Purreic acid contains $C_{21}H_{18}O_{11}$, purrenone $C_{20}H_{12}O_6$. By the action of chlorine, bromine, and nitric acid, a series of substitution-products are formed.

Frangulin, $C_6H_6O_3$, from *Rhamnus frangula*, has been already mentioned as a triatomic phenol (p. 571).

Morindin, $C_{28}H_{30}O_{15}$, is a yellow crystalline coloring matter, occurring in the root of *Morinda citrifolia*, called *Soranjee* in the East Indies. When heated it is converted into a beautiful crystalline body, *morindone*, containing $C_{14}H_{10}O_5$.

Aloes.—Certain of the products of the action of nitric acid upon *aloes*, very much resemble some of the derivatives of indigo, without, however, it seems, being identical with them. Powdered aloes, heated for a considerable time with excess of moderately strong nitric acid, yields a deep-red solution, which, on cooling, deposits a yellow crystalline mass. This, purified by suitable means, constitutes *chrysammic acid:* it crystallizes in golden-yellow scales, which have a bitter taste, and are but sparingly soluble in water. Its potassium-salt has a carmine-red tint, and exhibits a green metallic lustre, like that of murexide. The formula of chrysammic acid is not perfectly established. It is probably $C_7H_2N_2O_6$ or $C_7H_2(NO_2)_2O_2$. Like picric acid, it yields, with chloride of lime, *chloropicrin*. The mother-liquor, from which the chrysammic acid has been deposited, contains a second acid, the *chrysolepic*, which also forms golden-yellow, sparingly soluble, scaly crystals. The potassium-salt forms small, yellow prisms, of little solubility. It explodes by heat. Chrysolepic acid contains $C_6H_3N_3O_7$: it is said to be identical with picric acid.

To these may be added the *styphnic*, or *oxypicric acid*, described by Böttger and Will, produced by the action of nitric acid of sp. gr. 1·2 upon *assa-fœtida* and several other gum-resins and extracts. Brazil-wood and purree, when treated with excess of nitric acid, likewise yield styphnic acid. It crystallizes, when pure, in slender, yellowish-white prisms, sparingly soluble in water, readily dissolved in alcohol and ether. It has a purely astringent taste, and stains the skin yellow. By a gentle heat it melts, and on cooling becomes crystalline; suddenly and strongly heated it burns like gun-powder. It also yields chloropicrin. The salts of this substance mostly crystallize in orange-yellow needles, and explode with great violence by heat. Styphnic acid contains $C_6H_3N_3O_8$, *i. e.*, picric acid + 1 atom of oxygen.

RESINS AND BALSAMS.

Common resin, or *colophony*, furnishes perhaps the best example of the class. It is the resinous substance which remains when turpentine or pine resin is heated till the water and volatile oil are expelled, and is a mixture of two distinct bodies having acid properties: viz., *abietic acid*, $C_{44}H_{64}O_5$, which is crystallizable, and *pinic acid*, $C_{20}H_{30}O_2$, which is amorphous. These acids may be separated from each other by their difference of solubility in cold and somewhat dilute alcohol, the latter being by far the more soluble of the two. Pure abietic acid crystallizes in small, colorless, rhombic prisms, insoluble in water, soluble in hot strong alcohol, in volatile oils, and in ether. It melts when heated, but cannot be distilled without decomposition. An alcoholic solution of abietic acid, precipitated by sulphuric acid, yields another crystalline acid called *sylvic acid*, isomeric with pinic acid. A fourth resin-acid, called *pimaric acid*, also isomeric with pinic acid, has been found in the turpentine of the *Pinus maritima* of Bordeaux.

Lac is a very valuable resin, much harder than colophony, and easily soluble in alcohol: three varieties are known in commerce — viz., *stick-lac*, *seed lac*, and *shellac*. It is used in varnishes, and in the manufacture of hats, and very largely in the preparation of sealing-wax, of which it forms the chief ingredient. Crude lac contains a red dye called *lac-dye*, which is partly soluble in water. Lac dissolves in considerable quantity in a hot solution of borax; Indian ink, rubbed up with this liquid, forms a most excellent *label-ink* for the laboratory, as it is unaffected by acid vapors, and, when once dry, becomes nearly insoluble in water.

Mastic, *dammar-resin*, and *sandarac* are resins largely used by the varnish-maker. *Dragon's blood* is a resin of deep-red color. *Copal* is also a very valuable substance: it differs from the other resins in being but slowly dissolved by alcohol and essential oils. It is miscible, however, in the melted state with oils, and is thus made into varnish. *Amber* appears to be a fossil resin; it is found accompanying brown-coal or lignite. *Caoutchouc* and *gutta percha* have been already described as terpenes (p. 492).

Most of the resins, when exposed to destructive distillation, yield oily pyro-products, usually of hydrocarbons, which have been studied with partial success. Great difficulties occur in these investigations: the task of separating from each other, and isolating bodies which scarcely differ but in their boiling points, is exceedingly troublesome.

Balsams are natural mixtures of resins with volatile oils. They differ very greatly in consistence, some being quite fluid, others solid and brittle. By keeping, the softer kinds often become hard. Balsams may be conveniently divided into two classes — viz., those which, like *common* and *Venice turpentine*, *Canada balsam*, *Copaiba balsam*, &c., are nearly natural varnishes, or solutions of resins in volatile oils, and those which contain benzoic or cinnamic acid in addition, as *Peru* and *Tolu balsams*, and the solid resinous *benzoin*, commonly called *gum-benzoin*.

Tolu-balsam, by distillation with water, yields three products — namely, benzoic acid, cinnamein, or styracin, $C_{16}H_{44}O_2$ (p. 641), and *tolene*, a volatile, colorless hydrocarbon, boiling at 170° C. (338° F.), and containing $C_{12}H_{18}$, or, according to some authorities, $C_{10}H_{16}$. The balsam freed in this manner from essential oils, and exposed to destructive distillation, yields in succession a viscous liquid, which crystallizes in the receiver, and a thin liquid heavier than water; carbon dioxide and carbon monoxide are largely evolved, and the retort is afterwards found to contain a residue of charcoal. The solid product is chiefly a mixture of benzoic and cinnamic acids: the volatile oil contains at least two substances differing in their boiling points, and are easily separated — namely, *toluene* (p. 495), and an oily liquid

heavier than water, of high boiling point, and having the composition and characters of benzoic ether.

Liquid storax, distilled with water holding in solution a little sodium carbonate, yields a small and variable quantity of volatile oil, not homogeneous, but from which, by careful distillation, pure cinnamene or styrolene, C_8H_8 (p. 501), may be extracted.

Storax, from which the styrol has been separated by distillation, when treated with sodium carbonate, yields a considerable quantity of sodium cinnamate. The residue consists of resinous bodies, associated with styracin or cinnyl cinnamate (p. 641).

PART IV.

ANIMAL CHEMISTRY.

INTRODUCTION.

ANIMAL CHEMISTRY, for the purpose of clearness, may be divided into the chemistry of separate substances entering into the composition of the fluids and solids of animals, the chemistry of the complex animal fluids and textures, and the chemistry of the processes which take place in the animal body.

This classification has a great many advantages, and in the following brief abstract the subject will be considered under these different heads.

Many animal substances have been already fully mentioned in the inorganic part of this work: for example, water, carbonic acid, and calcium phosphate; the other animal substances, as urea, formic, and hippuric acid, have been placed in the organic part, because, from their composition, relations, and properties, they could not be separated from many bodies which are not connected with animal chemistry. As the chemical knowledge of other animal substances is perfected, these also will be placed under the head of organic chemistry; and thus animal chemistry will ultimately embrace the knowledge of the composition and properties of the complex fluids and textures of the body, and of the chemical actions resulting from the air and food which are requisite for the support of animal life.

Although animal chemistry has hitherto occupied the attention of nearly every great chemist, yet comparatively much remains to be done and to be undone. For example, the very different substances which are included under the term protein-principles, that is, of which protein is the first product of decomposition and ammonia carbonate the last, can scarcely yet be arranged according to their percentage-composition, much less be represented truly by any formulæ. The chemical composition of the different organs and textures of the body, of the brain or blood, for instance, or even of the bones, is differently given, according as this or that method of analysis is followed. The same may be said of the secretions and excretions; and these vary so much at different times, in different persons, and in different classes of animals, that no single standard of comparison can be adopted; but the highest and lowest limits of composition for health and disease must be regarded, and not the mean of a number of analyses.

A still more difficult problem is presented to the chemist in the investigation of the processes which take place in the bodies of animals and vegetables. The solution of the food by the action of alkalies, acids, and ferments; the nutrition of the organs by the blood; the production of animal heat by the action of inspired oxygen; and the removal from the body of the substances that have been used or are useless or injurious; — these are questions which in future years will form the chief subjects of investigation in animal chemistry, whilst in vegetable chemistry the influence of sunlight in promoting the formation of the innumerable compounds of carbon will have to be determined.

ON SEPARATE SUBSTANCES ENTERING INTO THE COMPOSITION OF THE FLUIDS AND SOLIDS OF ANIMALS.

ALBUMINOUS PRINCIPLES.

Although, in the present state of our knowledge, no chemical distinction exists between vegetable and animal substances, and although many mineral substances always exist in the fluids and solids of animals and vegetables, yet there is a class of substances which formerly were considered as exclusively animal, and of these we still know so little that it is most convenient still to keep them distinct from other organic substances. They form the chief part of the solid constituents of the blood, muscles, nerves, glands, and other organs of animals, and they occur in small quantities in almost every part of vegetables. Their atomic weight and constitution are still unknown, and only slight differences exist in the percentage composition; thus:

C	52,7	to	54,5
H	6,9	"	7,3
N	15,4	"	16,5
O	20,9	"	23,5
S	0,8	"	1,6

They are amorphous, more or less soluble in water, soluble in excess of acetic acid, more soluble in alkalies, almost insoluble in alcohol, and quite so in ether. Strong mineral acids dissolve all albuminous substances. The hydrochloric acid solution is first blue, then violet, then brown. The nitric acid solution is yellow, and gives rise to *xanthoproteic acid*, which dissolves in alkalies and ammonia with orange-red color. Caustic alkalies decompose albuminous substances according to the temperature, giving rise to leucine, tyrosine, oxalic acid, carbonic acid, and ammonia.

Albuminous substances are precipitated from solutions: 1. By excess of mineral acids. 2. By potassium ferrocyanide with acetic acid or a little hydrochloric acid. 3. By acetic acid, with a considerable quantity of concentrated solutions of neutral salts of alkalies and alkaline earths, gum arabic, or dextrin. When examined for circular polarization, they rotate the light more or less to the left.

Serum Albumin is the most abundant albuminous substance in animal bodies. It can be obtained tolerably pure from blood-serum by precipitation with lead acetate, washing with water, suspending the precipitated lead compound in water, and decomposing it with carbonic acid; then, by filtration, a very cloudy solution of albumin is obtained. It forms a yellow, elastic, transparent substance, which when perfectly dry can be heated to 100° without change. It is soluble in water and precipitable by alcohol; long continued action of alcohol changes it into coagulated albumin. Serum albumin is not precipitated by carbonic, acetic, tartaric, or phosphoric acid; when mixed with a very small quantity of other very weak

mineral acids, it is not precipitated; by large quantities of acid it is immediately precipitated; nitric acid acts most strongly. The precipitate with strong hydrochloric acid dissolves in an excess of acid; and on adding water to this solution, a precipitate forms, which, after filtration and squeezing, dissolves in water and has all the reactions of hydrochloride of syntonin; caustic potash and soda-solution change the serum albumin into compounds of albumin with the alkali.

When heated to 72° or 73° C. (163° F.), blood-serum coagulates into a compact mass. The fluid begins to be cloudy at 60° C. (140° F.). Coagulation occurs at a lower temperature when very dilute phosphoric or acetic acid is added, or neutral salts in small quantity, and at a higher temperature with a very little sodium carbonate.

Serum albumin is precipitated from its solutions by most of the salts of the heavy metals. When agitated with ether it does not coagulate.

Egg Albumin differs from serum albumin by gradually giving a precipitate when agitated with ether; oil of turpentine also coagulates this kind of albumin. Serum albumin dissolves easily in strong nitric acid, whilst egg albumin scarcely dissolves at all. When a solution of egg albumin is injected into the veins or under the skin of dogs or rabbits, the egg albumin passes unchanged into the urine, whilst serum albumin, injected in the same way, does not pass into the urine at all.

When white of egg is thinly spread upon a plate and exposed to evaporation in a warm place, it dries up to a pale-yellow, brilliant, gum-like substance destitute of all traces of crystalline structure. In this state it may be preserved unchanged for any length of time, the presence of water being in all cases necessary to putrefactive decomposition. The watery solutions of egg albumin and serum albumin coagulate at the same temperature under similar circumstances. The existence of unoxidized sulphur in albumin is easily shown; a boiled egg blackens a silver spoon, from a trace of alkaline sulphide formed or separated during the coagulation; and a solution of albumin in excess of caustic potash mixed with a little acetate of lead, gives, on boiling, a black precipitate containing sulphide of lead.

Casein; and Albuminate or Protein. — Albuminous substances, when treated with solution of potash, undergo more or less change according to the strength of the potash and the temperature at which the action takes place. Sometimes bodies can be produced which agree well together, and cannot be distinguished from the casein of milk, although most probably casein is not identical with artificial albuminate, and the bodies which are produced by the action of potash on different albuminous substances may differ slightly one from the other, as is evident in the difference of their rotatory action on polarized light.

Casein occurs most plentifully in the milk of animal feeders. In the fluids of the textures it has certainly not been found. In the blood it is entirely absent, and it is rarely present in the fluid of cysts.

It is best obtained from milk by precipitating it with crystalline magnesium sulphate, filtering and washing with a concentrated solution of Epsom salt, then dissolving the precipitate in water; the butter is filtered off, and the clear solution precipitated by dilute acetic acid.

For preparing protein or potassium albuminate, any albuminous substance may be used. Lieberkühn directs egg albumin to be stirred with an equal volume of water and filtered; the filtrate to be reduced to one-half in shallow vessels at 40° C. (104° F.), and, after cooling, to be mixed with concentrated potash drop by drop until the whole substance sets to a strong transparent jelly. This is cut into pieces of the size of a bean, and thrown into much distilled water; after being stirred, the water is poured off from the albuminate. The washing is repeated as long as any alkaline

reaction remains. The purified albuminate is then dissolved in boiling water or spirits of wine, in which it ought to give a clear solution.

An albuminate is more simply obtained by shaking milk with caustic soda and ether, pouring off the clear alkaline lower layer of fluid, precipitating it with acetic acid, and washing it with water.

The dried casein and albuminate are yellow, transparent, and hygroscopic, swelling up in water, but not dissolving. When precipitated in a flocky state, they dissolve easily in water if it contains a little alkali. The precipitate which forms on neutralizing the alkaline solution, dissolves easily in an excess of acetic acid or dilute hydrochloric acid. On the addition of an excess of mineral acid, or by neutralizing with an alkali, these solutions give a precipitate.

The neutral or feebly alkaline albuminate and casein in alkaline solution, are precipitated in the cold by alcohol: when hot they are dissolved. Albuminates are precipitated by copper sulphate, silver nitrate, and barium chloride. Lieberkühn gives as their formula $C_{72}H_{112}R_2N_{18}O_{23}S$, R denoting an atom of univalent metal. According to him, potassium albuminate has the same composition. Meissner says that by boiling casein continuously, lactic acid and creatin are formed.

By fusion with potassium hydrate, casein yields valeric and butyric acids, besides other products.

The most striking property of casein is its coagulability by certain animal membranes. This is well seen, in the process of cheesemaking, in preparing the *curd*. A piece of the stomach of the calf, with its mucous membrane, is slightly washed, put into a large quantity of milk, and the whole slowly heated to about 53° C. (124° F.). In a short time after this temperature has been attained, the milk is observed to separate into a solid, white coagulum, or mass of curd, and a yellowish, translucent liquid called *whey*. The curd contains all the casein of the milk, much of the fat, and much of the inorganic matter: the whey retains the milk-sugar and the soluble salts. It is just possible that this mysterious change may be really due to the formation of a little lactic acid from the milk-sugar, under the joint influence of a slowly decomposing membrane and the elevated temperature, and that this acid may be sufficient in quantity to withdraw the alkali which holds the casein in solution, and thus occasion its precipitation in the insoluble state. The loss of weight the membrane itself suffers in this operation is very small: it has been found not to exceed $\frac{1}{1800}$ part.

Paralbumin has as yet been found only in ovarian cysts, and it rarely occurs alone. It is precipitated by alcohol, but still contains some alkali. It is coagulated by boiling, but cannot be filtered. When it is dissolved in much water, and carbonic acid gas is passed through it, a plentiful flocky precipitate falls; acetic acid carefully added acts still better. The precipitate is easily soluble in an excess of acetic acid, or in a very weak solution of alkali. By the addition of magnesium sulphate it is not precipitated from a feeble alkaline solution. It gives a precipitate with acetic acid and potassium ferrocyanide, lead acetate, alum, and copper sulphate. The composition of this albuminous substance is stated by Haerlin to be 51·8 carbon, 6·9 hydrogen, 12·8 nitrogen, 26·8 oxygen, and 1·7 sulphur.

Syntonin or Parapeptone. — As by the action of alkalies on albuminous matters the albuminates are produced, so by treating these with strong hydrochloric acid, syntonin is formed among other products of decomposition. Probably the shorter the time the acid is in action, the more syntonin is formed. It is also formed from other albuminous substances, most easily from myosin, as in the first action of the gastric juice in the stomach. For preparing syntonin, fresh-cut meat is treated with cold water, and the residue is mixed with water containing $\frac{1}{1000}$ hydrochloric acid; a thick-

ish solution is thus obtained which can be filtered. The clear liquid is carefully neutralized with sodium carbonate, which gives a gelatinous precipitate of syntonin; this is purified by washing with water, alcohol, and ether. It contains much unaltered myosin. From fibrin, serum albumin, or any other albuminous matter, except uncoagulated egg albumin, syntonin may be obtained by dissolving them in fuming hydrochloric acid, filtering, and precipitating the filtrate with twice its volume of water; the precipitate is filtered off, dissolved in water, and precipitated by careful neutralization with sodium carbonate.

The composition of syntonin is 54·1 carbon, 7·3 hydrogen, 16·1 nitrogen, 21·5 oxygen, and 1·1 sulphur. It is insoluble in solution of sodium chloride, whatever its concentration; easily soluble in dilute hydrochloric acid, and in feebly alkaline liquids. The solution in lime-water is partially coagulated by boiling. When the solution is boiled, sodium chloride, magnesium sulphate, or calcium chloride, gives a precipitate as with many other albuminous substances. Syntonin, like casein, when dissolved in very dilute hydrochloric acid, gives a precipitate with neutral potassium-salts at ordinary temperatures. By the action of strong hydrochloric acid on uncoagulated albumin, an albuminous substance is first obtained, which is scarcely soluble in water, and is also very slightly soluble in dilute hydrochloric acid.

Myosin was first separated by Kühne from other albuminous matters occurring in the protoplasma or contractile muscular substance that causes the *rigor mortis*. To prepare it well, cut-up flesh is carefully washed with water, and the mass is then placed in a mixture of one volume of concentrated solution of common salt to two volumes of water; these are continually rubbed together and filtered through linen; the slimy filtrate is allowed to drop into much distilled water. The myosin is re-dissolved in solution of sodium chloride, and re-precipitated by much water. It is insoluble in water, soluble in solution of common salt under 10°, soluble in very dilute hydrochloric acid, but in this solution it passes by degrees into syntonin; in dilute alkali, myosin, like other albuminous matter, is soluble, being changed into albuminate. By heat it is changed into coagulated albumin. It is also coagulated by alcohol. The substances which occur in yolk of egg, the crystalline lens, and the fluid from some cysts, soluble in concentrated solutions of common salt, but not soluble in water, have been considered by Denis as identical with myosin, called by him globulin.

Fibrino-plastic Substance and Fibrinogen, or Paraglobulin, or Paraglobin.—Alexander Schmidt has found that fibrin is formed by the contact of two albuminous matters. One he calls fibrinoplastic and the other fibrinogenous substance. The first is especially plentiful in the red blood-globules, in the serum of the blood, the cellular tissue, and the cornea. The second is found in exudations, specially in the pericardium and fluid of hydrocele, in lymph and chyle. In their reactions they nearly resemble myosin, being soluble in a solution of common salt, and precipitable by an excess of it. They dissolve in very dilute hydrochloric acid, and, by keeping, change into a syntonin-like substance; soluble also in very feeble alkaline solutions, from which the fibrinoplastic substance is more easily precipitated than the fibrinogenic by carbonic acid. When these two substances come into contact in any fluid, they combine, quickly or slowly, according to the greater or less quantity of each substance in the fluid, to form *Fibrin*. The fluid coagulates either to a mass of jelly, or, when very little is present, the fibrin forms in separate flocks. The coagulation takes place more quickly at a high temperature, more slowly at a low temperature. The temperature of the blood appears peculiarly adapted for quick coagulation; whereas at 0° C. it is as slow as possible. In the living vessels

the blood coagulates slowly; by contact with foreign bodies coagulation occurs quickly. Carbonic acid protracts or prevents coagulation; passing air through the liquid, or any other agitation, hastens it. Free acids, for example, acetic, lactic, phosphoric, and also free alkalies and their carbonates, stop coagulation. When brought into a solution of sodium nitrate or chloride, fibrin swells to a slimy jelly-like mass, and partially dissolves: sodium sulphate also hinders the coagulation of fibrin. Thus fibrin may be prepared by allowing the blood to flow from a vein into a vessel containing much concentrated solution of sodium sulphate whilst it is briskly stirred. The whole is left to stand until the blood-globules are completely separated. The clear fluid is then thrown into ten times its bulk of water, on which the coagulation of the liquid takes place. When washed fibrin in a neutral liquid is heated to 72°, it becomes white and loses its transparency, like coagulated albumin. If the liquid has an acid reaction, the coagulation takes place even at a lower temperature. Fibrin is usually procured by washing the coagulum of blood in a cloth until all the soluble portions are removed, or by agitating fresh blood with a bundle of twigs, when the fibrin attaches itself to the latter, and is easily removed and cleansed by repeated washing with water, after which the fat is extracted by ether. On an average, fibrin has the composition 52·6 carbon, 7·0 hydrogen, 17·4 nitrogen, 21·8 oxygen, and 1·2 sulphur.

Coagulated Albuminous Substances. — Coagulated albumin is formed from albumin, syntonin, fibrin, myosin, &c., by heating their neutral solutions to boiling, or by the action of alcohol. Egg albumin is also changed into coagulated albumin by strong hydrochloric acid and by ether. The albuminates, and also casein, when precipitated by neutralization, pass into coagulated albumin when heated. The coagulated albuminous substances are insoluble in water, alcohol, and other indifferent fluids, scarcely soluble in dilute potash, soluble with great difficulty in ammonia. In acetic acid they swell up, and by degrees dissolve. They are mostly insoluble in dilute hydrochloric acid; but when pepsin is also present at blood heat, they change first into syntonin, and then into peptone. They are dissolved by strong hydrochloric acid, and by caustic potash they are changed into albuminates.

Amyloid Substance.—According to C. Schmidt, Friedreich, and Kekulé, it is composed of 53·6 carbon, 7·10 hydrogen, 15·0 nitrogen, and 14·4 oxygen and sulphur. It differs only from coagulated albumin in being colored reddish by iodine, and violet by sulphuric acid and iodine. It gives no trace of sugar when boiled with dilute sulphuric acid, but with caustic potash and acid it behaves exactly like an albuminous substance. Concentrated hydrochloric acid dissolves it, and the solution diluted with water gives a precipitate which has all the properties of syntonin hydrochlorate. By solution in caustic potash, a potassium albuminate is obtained. It may be formed at will by treating fibrin with very dilute hydrochloric acid, and evaporating the solution to dryness in a water-bath. An impure amyloïd substance may be obtained from any gland much infiltrated with the substance, as, for example, the liver, by dividing it and removing the vessels, and extracting the bile substances with cold water. It is then boiled for some time with water to remove the cellular tissue, and the residue is treated with boiling alcohol and ether to dissolve the fat and cholesterin. The residual mass consists chiefly of amyloïd substance characterized by the iodine reaction.

Peptone. — By the action of the acid gastric juice, all albuminous substances are changed into bodies called peptones. These are found only in

the stomach and contents of the small intestines. They can no longer be detected in the chyle. They are easily soluble in water, insoluble in alcohol or ether; but alcohol separates them with difficulty from the watery solution; when precipitated they remain unchanged even after boiling. They are not precipitated either by acids or by alkalies. Acetic acid and potassium ferrocyanide give no precipitate; but corrosive sublimate and lead acetate with ammonia give precipitates. The substance designated by Meissner as *metapeptone* does not certainly belong to the peptones, although of these there are many different kinds, whose properties are not yet sufficiently made out to enable them to be accurately distinguished.

Metalbumin was found by Scherer in a slimy, ropy, dropsical liquid obtained by tapping. In the dilute liquid neither acetic nor hydrochloric acid caused a precipitate. It became cloudy when boiled, and after this acetic acid caused no precipitate. Acetic acid and potassium ferrocyanide also caused no precipitate. Alcohol caused a precipitate, which redissolved in water.

Hæmoglobin, 54·2 carbon, 7·2 hydrogen, 0·42 iron, 16·0 nitrogen, 21·5 oxygen, and 0·7 sulphur; also called *Hæmatoglobulin* and *Hæmatocrystallin*. This substance forms the chief part of the red globules of the blood of vertebrata; usually it is obtained in an amorphous condition, but from the blood of some animals — as, for example, dogs, cats, rats, mice, and many fish — it can be separated in the crystalline form. Red crystals can be obtained from dog's blood by mixing the defibrinated blood with an equal quantity of water and adding one volume of alcohol to four volumes of the diluted blood and leaving it to stand at 0° C., or lower. After twenty-four hours the crystals are filtered off, squeezed, and dissolved in the least possible quantity of water at 25° to 30° C. (77°–86° F.). This solution is again mixed with one-fourth its volume of alcohol, and the re-crystallization is repeated many times. In different animals differently formed crystals are found. In the guinea-pig they are tetrahedrons; in the squirrel, six-sided tables; in the goose, rhombic four-sided or six-sided tables; in dogs and cats, long four-sided prisms. In a vacuum over sulphuric acid they lose water of crystallization and change into a bright brick-red mass. The crystals which form when the air has access to them also contain oxygen loosely combined; the more moist they are the more oxygen they contain. This they lose when warmed in a vacuum; by exposure over sulphuric acid a portion of the oxygen escapes. The crystals dissolve in water with difficulty; the saturated solution at 5° C. (41° F.), contains 2 per cent. hæmoglobin, but by increase of temperature the solubility is considerably increased. In feebly alkaline liquids, as in blood-serum, the crystals are much more soluble.

These solutions have a very beautiful blood-red color and absorb the light from the commencement of the red to three-fourths of the section of the spectrum between the lines C and D in the solar spectrum. The part of the spectrum lying about the line D of this space between C and D is much more strongly absorbed than the rest. If the oxygen is expelled from the solution by carbonic acid or hydrogen, the liquid then absorbs the light most beyond D; the rest of the light is more strongly absorbed than it is by the hæmoglobin solution which contains oxygen; and even the light between A and B is more strongly absorbed by solutions which contain no oxygen than by those which contain it. The change of color and transparency of the blood and blood-solutions when they pass from the venous condition into one containing more oxygen, and *vice versâ*, depend, without doubt, on these optical properties. The fresh blood taken from a vein of an animal shows clearly strong absorption of light from B

to beyond C in the spectrum, and this disappears when the blood is agitated with air.

When a concentrated solution of hæmoglobin is diluted with water, it rapidly increases in transparency up to the line D; by further dilution the spectrum extends beyond F, whilst at the same time between D and E a green-yellow streak appears. The band lying nearest to D is darker and more sharply bounded than the other, and ultimately disappears by continued dilution a little later than the other band; the appearance of these bands is influenced by the combination of oxygen with the hæmoglobin. For if a tolerably dilute blood solution is allowed to stand some time, or if such a solution is warmed in a water-bath above 50° C. (122° F.), or if to a blood solution, or a pure solution of hæmoglobin, a few drops of ammonium sulphide, or of an ammoniacal solution of zinc tartrate, be added, the arterial color of the solution gradually vanishes, and by examination in the spectrum, in the place between these two bands, there is seen a broader ill-defined absorption-band, about in the middle between D and E; at the same time the blue shows that it is less absorbed than by blood containing oxygen. The venous blood of animals does not show this property clearly when it is taken from the animal; but animals that have died asphyxiated do show this change in the blood. If a solution of hæmoglobin, or of blood, from which the oxygen has been taken away, is shaken with atmospheric air, the two absorption-bands of the hæmoglobin containing oxygen again appear, and the oxygen must be chemically combined with the hæmoglobin, for it is not removed by nitric oxide gas.

Dilute solutions of hæmoglobin may be heated to 70° or 80° C. (158°–176° F.) for a short time without marked change, but when the heat is continued, the hæmoglobin splits into hæmatin and coagulated albumin, with marked change of color and coagulation. Alcohol causes the same decomposition. Generally no substance is known which can precipitate hæmoglobin without at the same time destroying it; alkalies, and more readily acids, cause it to split without first precipitating it; this occurs the more readily the more concentrated the alkali or acid is, or the greater the quantity of it used, and the more concentrated the solution of hæmoglobin, or the higher the temperature. Hæmoglobin, in a dilute solution at ordinary temperature, is not decomposed by carbonated alkalies. A feebly alkaline solution is more permanent than a neutral solution; the feeblest acids, even carbonic acid, decompose hæmoglobin; hydrogen sulphide does not act on hæmoglobin when it contains no oxygen, but on oxyhæmoglobin it acts, causing the separation of sulphur and of an albuminous substance. Carbon monoxide passed into a solution of oxyhæmoglobin drives the oxygen out and forms a compound of carbon monoxide and hæmoglobin. It also combines with hæmoglobin free from oxygen.

Metahæmoglobin, so named by Hoppe, may be a mixture of hæmatin and an easily soluble albuminous matter. It has been found in old extravasations of blood, in the brown fluid from the ovaries, in strumous cysts, hydrocele, &c., or when a solution of hæmoglobin is long kept. Even when a solution of hæmoglobin is filtered, that which is sucked up by the edge of the filter passes into metahæmoglobin. Ozone has the same action. A solution of metahæmoglobin has a manifestly acid reaction arising from volatile acids (butyric and formic), produced by changes in the hæmoglobin. The optical properties of metahæmoglobin are similar to those of solutions of hæmatin in acids, alcohol, and ether.

Hæmatin, $C_{96}H_{102}N_{12}Fe_2O_{18}$, occurs in the body as a product of the decomposition of hæmoglobin in old extravasations; after hæmorrhage into the stomach it may be found in the fæces. It is obtained pure by dissolving the compound with hydrochloric acid in ammonia, evaporating to dryness,

and heating the residue to 130° C. (266° F.). The ammonium chloride is extracted with water, and the residue dried at 130°. It gives 12·8 per cent. of iron oxide as a residue when burnt, and is insoluble in water, alcohol, ether, and chloroform. In ammoniacal solutions it is soluble. It combines with alkalies and acids: by boiling with dilute nitric acid it loses its color, and is decomposed. Chlorine passed into an alkaline solution decomposes it very rapidly.

Hæmatin combined with Hydrochloric Acid, $C_{96}H_{102}N_{12}Fe_3O_{18}.2HCl$, is obtained in regular crystals by treating hæmoglobin or metahæmoglobin with common salt and strong acetic acid. The defibrinated blood of some animal is diluted with once or twice its volume of water, and lead acetate is added as long as a precipitate falls. The blood is then filtered, and the excess of lead removed from the filtrate by sodium carbonate, again filtered, and the clear solution is evaporated over sulphuric acid. The residue is powdered and rubbed with from 15 to 20 times its weight of commercial glacial acetic acid, to which a little common salt is added. The brown mixture is heated in a water-bath, and frequently shaken for an hour or two until all is dissolved. About five times the volume of pure water is then added, and it is left to stand for a week in an even temperature. The liquid is then poured off from the crystals; these are again boiled with glacial acetic acid; a great mass of water is then added, and the precipitate is allowed to settle, separated, well washed, again allowed to deposit, and then dried in a water-bath. The crystals are mostly thin rhombic plates of dark-blue color, and dirty-brown by transmitted light. From the name of their discoverer they are called *Teichmann's Hæmin crystals*. They are perfectly insoluble in water, alcohol, and ether. They are soluble in acids and alkalies, but only in acetic and hydrochloric acids without decomposition. They may be heated to 130° C. (266° F.), without decomposition: at red heat they do not swell up, but burn, leaving pure oxide of iron.

Mucin, containing 52·2 carbon, 7·0 hydrogen, 12·6 nitrogen, and 28·2 oxygen, usually called mucus, may be prepared from filtered ox-gall by precipitating it with alcohol, washing with dilute alcohol, dissolving in water, and precipitating by acetic acid. It cannot be perfectly purified from biliary coloring matter. It may be obtained more pure from the salivary glands by solution in water and precipitation by acetic acid. Mucin swells up in water, and by sufficient dilution it can be filtered. It is precipitable by alcohol in excess; also by acetic acid, and it is not soluble in an excess of the precipitant; also by nitric, hydrochloric, and sulphuric acids, and it is soluble in an excess of these acids. It is not precipitated by mercuric chloride, lead acetate, or potassium ferrocyanide. It is not coagulable by boiling; when thoroughly dried, it merely swells in water to a thick mass.

Pyin is said often to occur in pus: but normal pus contains neither pyin nor mucin. It is precipitable by acetic acid, and this precipitate is not soluble in an excess of acid, while the precipitates with nitric and hydrochloric acids are so; a solution of pyin in hydrochloric acid is not precipitable by a solution of potassium ferrocyanide. It is distinguishable from mucin only by being precipitable by mercuric chloride and lead acetate. The precipitate which forms in the serum of healthy pus on the addition of acetic acid is soluble in a solution of common salt, and consists of albumin.

Pepsin has not yet been perfectly isolated; it resembles mucin, and is precipitated by lead acetate and by alcohol; according to Brücke's discovery it is also carried down from its solution when any fine granular precipitate is produced. Brücke's method has also been used for isolating other substances resembling pepsin. For this purpose fresh-formed cal-

cium phosphate or cholesterin is dissolved in 4 parts alcohol and 1 ether, or even animal charcoal or milk of sulphur may be used. The pepsin may be obtained thus dissolved in water, and this, when mixed with very dilute hydrochloric acid, changes albumin into peptone.

Sugar-forming Ferments in Saliva and Pancreatic Fluid have also been separated by addition of dilute phosphoric acid, and subsequent neutralization afterwards by lime-water and by ethereal solutions of cholesterin. They can be dissolved in water and precipitated by absolute alcohol. They can be dried at ordinary temperatures without decomposition. If heated to 100°, they lose their power of acting upon starch. When boiled with nitric acid, and mixed with an excess of ammonia, the solution remains colorless.

Gelatin and Chondrin.—Animal membranes, skin, tendons, and even bones, dissolve in water at a high temperature more or less completely, but with very different degrees of facility, giving solutions which on cooling acquire a soft-solid, tremulous consistence. The substance so produced is called *gelatin:* it does not pre-exist in the animal system, but is generated from the membranous tissue by the action of hot water. The jelly of calves' feet, and common size and glue, are familiar examples of gelatin in different conditions of purity. Isinglass, the dried swimming-bladder of the sturgeon, dissolves in water merely warm, and yields a beautifully pure gelatin. In this state it is white and opalescent, or translucent, quite insipid and inodorous, insoluble in cold water, but readily dissolving by a slight elevation of temperature. Cut into slices and exposed to a current of dry air, it shrinks prodigiously in volume, and becomes a transparent, glassy, brittle mass, which is soluble in warm water, but insoluble in alcohol and ether. By dry distillation a watery fluid is produced, containing much carbonate of ammonia, and a thick brown oil, in which, besides ammonium carbonate, ammonium sulphide, ammonium cyanide, and neutral oily bodies, various basic substances exist, as aniline, picoline, methylamine, trimethylamine, butylamine, and probably many others. In the dry state, gelatin may be kept indefinitely: in contact with water, it becomes acid, loses the property of gelatinizing, and putrefies. Long-continued boiling gradually alters it, and the solution loses the power of forming a jelly on cooling. 1 part of dry gelatin or isinglass dissolved in 100 parts of water solidifies on cooling.

An aqueous solution of gelatin is precipitated by alcohol, which withdraws the water: corrosive sublimate in excess gives a white flocculent precipitate, and the same happens with solution of mercurous and mercuric nitrate: neither alum, neutral lead acetate, nor basic lead acetate affects a solution of gelatin. With tannic acid or infusion of galls, gelatin gives a copious, whitish, curdy precipitate, which coheres on stirring to an elastic mass, quite insoluble in water, and incapable of putrefaction.

Tannic acid is the only acid that gives a precipitate with a solution of gelatin. It does so even when the solution is exceedingly dilute.

Chlorine passed into a solution of gelatin occasions a dense white precipitate of *chlorite of gelatin,* which envelops each gas-bubble, and ultimately forms a tough, elastic, pearly mass, somewhat resembling fibrin. Boiling with strong alkalies converts gelatin, with evolution of ammonia, into leucine, and glycocine. This last-mentioned substance, also called *glycocol,* was first formed by the action of cold concentrated sulphuric acid upon gelatin, and has lately been obtained by the action of acids upon hippuric acid, which is thereby resolved into benzoic acid and glycocine (see page 633).

A dilute solution of gelatin, distilled with a mixture of potassium bichro-

mate and sulphuric acid, yields acetic, valeric, benzoic, and hydrocyanic acids, and two volatile oily principles termed *valeronitrile*, C_5H_9N, and *valeracetonitrile*, $C_{26}H_{48}N_4O_6$. The former is a thin colorless liquid, of aromatic odor, like that of salicylol: it is lighter than water, and boils at 125° C. (257° F.). The latter much resembles the first, but boils at 70° C. (158° F.). Alkalies convert valeronitrile into valeric acid and ammonia, and valeracetonitrile into valeric acid, acetic acid, and ammonia. Valeracetonitrile contains the elements of 4 molecules of valeronitrile and 3 molecules of acetic acid:

$$C_{26}H_{48}N_4O_6 \quad = \quad 4C_5H_9N \quad + \quad 3C_2H_4O_2.$$

Dry gelatin, subjected to analysis, has been found to contain in 100 parts, 50·05 carbon, 6·47 hydrogen, 18·35 nitrogen, and 25·13 oxygen.

The cartilage of the ribs and joints yields a gelatin differing in some respects from the preceding: it is called, by way of distinction, *chondrin*. It is less soluble in boiling water than gelatin. It is precipitated from its solution by acetic acid, and is not soluble in an excess of acid. Other acids in very small quantity precipitate chondrin, but the slightest excess redissolves the precipitate. Acetate of lead and solution of alum also precipitate this substance. These reactions distinguish chondrin from gelatin. Scherer gives 50·75 carbon, 6·90 hydrogen, 14·70 nitrogen, and 27·65 oxygen. The doubtful formulæ $C_{16}H_{26}N_4O_7$ and $C_{24}H_{40}N_6O_{10}$, have been assigned to chondrin.

If a solution of gelatin, albumin, fibrin, casein, or probably any one of the more complex azotized animal principles, be mixed with solution of cupric sulphate, and then a large excess of caustic potash added, the greenish precipitate first formed is redissolved, and the liquid acquires a deep and beautiful purple tint.

Gelatin is largely employed as an article of food, as in soups, &c.; but its value in this respect has been perhaps overrated. In the useful arts, size and glue are consumed in great quantities. These are prepared from the clippings of hides, and other similar matters, enclosed in a net, and boiled with water in a large caldron. The strained solution gelatinizes on cooling, and constitutes *size*. Glue is the same substance in a state of desiccation, the size being cut into slices and placed upon nettings freely exposed to a current of air. Gelatin is extracted from bones with much greater difficulty: the best method of proceeding is said to be to enclose the bones, previously crushed, in strong metallic cylinders, and admit high-pressure steam, which attacks and dissolves the animal matter much more easily than boiling water; or, to steep the bones in dilute hydrochloric acid, thereby removing the earthy phosphate, and then dissolve the soft and flexible residue by boiling.

There is an important economical application of gelatin, or rather of the material which produces it, which deserves notice — viz., to the clarifying of wines and beer from the finely divided and suspended matter which often renders these liquids muddy and unsightly. When isinglass is digested in very dilute cold acetic acid, as sour wine and beer, it softens, swells, and assumes the aspect of a very light transparent jelly, which, although quite insoluble in the cold, may be readily mixed with a large quantity of watery liquid. Such a preparation, technically called *finings*, is sometimes used by brewers and wine-merchants for the purpose before mentioned: its action on the liquor with which it is mixed seems to be purely mechanical, the gelatinous matter slowly subsiding to the bottom of the cask, and carrying with it the insoluble substance to which the turbidity was due.

Horny Matter; Elastin (55·5 carbon, 7·4 hydrogen, 16·7 nitrogen, and 20·5 oxygen). — This substance is prepared by boiling the *ligamentum nuchæ*

of cattle with alcohol, ether, water, concentrated acetic acid, and dilute caustic soda. It has a yellow color when moist, is extensible, but becomes brittle after drying. It is perfectly insoluble in cold or boiling water, also in ammonia, acetic acid, or alcohol. In a concentrated solution of potash it is dissolved, and at the same time decomposed. The solution is not precipitated by acids, only with tannic acid the neutral solution gives a precipitate. When boiled with sulphuric acid it is decomposed, with formation of leucine.

Keratin. — Hair, nails, horn, feathers, epidermis, and epithelium, boiled with ether, alcohol, water, and dilute acid, yield residual substances which do not agree well in their analysis, and therefore probably are not rightly classed under one name. These bodies swell but little in water, but when dry are very hygroscopic. By continual boiling in water at 150° C. (302° F.), they partially decompose. A milky liquid forms, and sulphuretted hydrogen escapes. If the solution is evaporated to dryness, a residue, insoluble in water, remains. In acetic acid these substances swell up more than in water, without materially altering in texture; in concentrated acetic acid they dissolve when boiled; and when boiled with sulphuric acid, they give leucine, and about 4 per cent. of tyrosine. In caustic potash, and with difficulty in a solution of potassium carbonate, they swell up, and when heated dissolve. The alkaline solutions evolve sulphuretted hydrogen on addition of acids.

Fibroïn, 48·6 carbon, 6·5 hydrogen, 17·3 nitrogen, and 27·6 oxygen. — This substance dissolves in concentrated acids and alkalies and in ammoniacal cupric solution, but not in ammonia: when neutralized, the solutions give precipitates; by boiling with dilute sulphuric acid it yields leucine and 5 per cent. of tyrosine.

Spongin is obtained from sponge by treating it with ether, alcohol, hydrochloric acid, and 5 per cent. soda-lye. It closely agrees in composition with fibroïn, but when boiled with sulphuric acid does not yield tyrosine, but glycocine and leucine.

Conchiolin forms the greater part of the organic basis of mussel-shells. It is insoluble in water, alcohol, acetic acid, dilute mineral acid, and potash-lye. It contains 16 or 17 per cent. of nitrogen, and gives by boiling with sulphuric acid, only leucine, and no tyrosine, glycocine, or sugar.

Chitin, from the skeleton of insects and crustacea, $C_9H_{12}HO_6$. It is best prepared by boiling the elytra of the cockchafer with alkalies, water, acetic acid, alcohol, and ether. It yields glucose when dissolved in sulphuric acid.

Protagon and Eurine. — Protagon, first prepared and investigated by Liebreich, was formerly known in an impure state as cerebrin, cerebric acid, lecithin, and when swollen in water, as myelin. It forms the chief constituent of the nervous substance in the nervous centres and peripheral nerves. It also most likely occurs in oil of eggs, in pus-cells, in white blood-cells, and in semen; but at present it has only been obtained pure from the brain, which must be freed as much as possible from blood and extraneous tissues. The emulsion is agitated with water, and poured into a flask: much ether is poured on it, and after constant shaking at 29° C. (84° F.), it is allowed to stand for some time and at the same temperature. The ether is poured off, filtered, and the solution is cooled from 0° to — 10° C. (14° F.), filtered at this low temperature, and washed out with cold ether until no more cholesterin is extracted by the ether. The residue is dried over sulphuric acid, dissolved in alcohol of 80 per cent. at 40° C. (104° F.), to form a not too concentrated solution, and then it is allowed to cool slowly in a water-bath. The protagon crystallizes out in

bundles of fine needles. It is colorless and without smell, scarcely soluble in pure ether, easily in warm spirit of wine, very easily in fatty and ethereal oils, and very easily also in warm ethereal solutions of fat. In water it swells up to an opalescent white mass like a decoction of starch, and in concentrated solution forms a firm paste. When heated in alcohol, more especially in absolute alcohol, above 50° to 60° C. (122°–140° F.), it decomposes with separation of oily drops. When boiled with strong baryta-water, the protagon by degrees decomposes into glycerin, phosphoric acid, stearic acid, and a third crystalline non-nitrogenous acid not thoroughly investigated; but its lead-salts are soluble in ether; in addition to these acids, neurine is formed, which is a strong base.

Neurine, $C_5H_{15}NO$, or $C_5H_{14}N(OH)$, was obtained by Liebreich by boiling protagon continuously with baryta-water, precipitating the baryta with carbonic acid, evaporating the filtrate to a very small volume, precipitating with absolute alcohol, evaporating the filtered alcoholic extract to a syrup, again dissolving it in absolute alcohol, and precipitating the concentrated solution in alcohol with platinic chloride. The double platinum-salt, $(C_5H_{14}NCl)_2 . PtCl_4$, is easily soluble in water, and crystallizes in thin large rhombic tables of a yellow color. It is not altogether insoluble in alcohol. Solutions of neurine react very strongly alkaline, even after carbonic acid has long been passed into them. The solution of the base in absolute alcohol becomes thick by passing carbonic acid into it; carbonate of neurine with an alkaline reaction then forms. This is decomposed with effervescence by strong acids. The neurine forms out of protagon by simply splitting into glycerin, phosphoric acid, &c. By its formation no evolution of ammonia takes place, and the neurine takes all the nitrogen of the protagon. Bauer has lately shown that this substance is the hydrate of trimethyl-ethyl-ammonium, and Wurtz has actually produced this complex organic substance synthetically.

Inosinic Acid, $C_5H_8N_2O_6$ (?), found by Liebig in the flesh of some warm-blooded animals. It has not yet been obtained in crystals, but as a syrup which becomes solid in alcohol. It dissolves easily in water, reddens litmus strongly, tastes pleasantly like soup, and partly decomposes by boiling. Its salts, even those of the alkalies, are crystalline. The alkaline salts are soluble in water. The copper and silver-salts form amorphous, insoluble, or almost insoluble precipitates. In alcohol and ether the inosinic salts are not soluble.

Chlorohodic Acid, obtained by Bœdecker from pus by extraction with ether, alcohol, and water, precipitation with lead acetate, decomposition by hydrogen sulphide, and extraction with absolute alcohol, forms fine microscopic needles. The acid dissolves easily in water or alcohol, but not in ether. It will not sublime, melts when heated, and burns, with the smell of horn. In its watery solutions, chloride of mercury and tin and nitrate of mercury cause a white precipitate. So also does tannin. Iodine gives a light yellow precipitate. Chlorine water in dilute solutions gives a rose-red color; dark-red in concentrated solutions.

Excretin, $C_{78}H_{156}O_2S$, according to Marcet. Alcoholic extract of human fæces is precipitated with lime, and extracted with alcohol and ether, and the solution left at a sufficiently low temperature to crystallize. It melts at 92° to 96° C. (198°–205° F.), is soluble in water, and in warm alcohol or ether, almost insoluble in cold alcohol. The solutions have a neutral reaction. Neither boiling caustic potash nor dilute acids attack it. Nitric acid easily decomposes it.

Excretolic acid is the name given by Marcet to a mixture of fatty acids, &c., which are precipitated from the alcoholic extract of excrement by lime.

ON THE ANIMAL FLUIDS.

BLOOD, URINE, SWEAT, SALIVA, GASTRIC JUICE, BILE, CHYLE, MUCUS, PUS, MILK.

Composition of the Blood. — The blood is the general circulating fluid of the animal body, the source of all nutriment and growth, and the general material from which all the secretions, however much they may differ in properties and composition, are derived. Food or nourishment from without can only be made available by first passing through the blood. It serves also the scarcely less important office of removing and carrying off from the body principles which are hurtful, or no longer required.

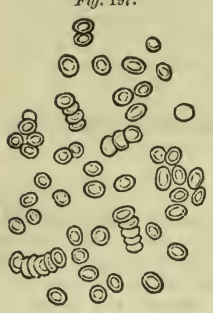
In all vertebrated animals the blood has a red color, and probably in all cases a temperature above that of the medium in which the creature lives. In the mammalia this is very apparent, and in the birds still more so. The heat of the blood is directly connected with the degree of activity of the respiratory process. In man the temperature of the blood seldom varies much from 36·6° C. (98° F.), when in a state of health, even under great vicissitudes of climate: in birds it is sometimes as high as 42·8° C. (109° F.). To these two highest classes of the animal kingdom, the mammifers and the birds, the observations about to be made are intended especially to apply.

In every creature of this description two kinds of blood are met with, which differ very considerably in their appearance, viz., that contained in the *left* side of the heart and in the arteries generally, and that contained in the *right* side of the heart and in the veins: the former, or *arterial* blood, has a bright-red color; the latter, the *venous* blood, is blackish-purple. The conversion of the dark into the florid blood may be traced to what takes place during its exposure to the air in the lungs; and the opposite change, to what takes place in the capillaries of the general vascular system, or the minute tubes or passages, distributed in countless numbers throughout the whole body, which connect the extremities of the arteries and veins. When compared together, little difference of properties or composition can be found in the two kinds of blood: the hæmoglobin of arterial blood is found by spectrum analysis to differ from the hæmoglobin of venous blood. The difference in the interference bands is caused by the combination of oxygen with hæmoglobin in the arteries and its deoxidation in the veins. The fibrin varies a little, that from venous blood being, as already mentioned, soluble in a solution of potassium nitrate, which is not the case with arterial fibrin. It is, besides, very prone to absorb oxygen, and to become, in all probability, partly changed to a higher oxygen-compound of fibrin. The only other notable point of difference is in the gaseous matter the blood holds in solution, carbonic acid predominating in the venous, and free oxygen in the arterial variety.

In its ordinary state the blood has a slimy feel, a density varying from 1·053 to 1·057, and a decidedly alkaline reaction, partly from soda combined with albumin, and partly from sodium carbonate and phosphate: it has a saline and disagreeable taste, and, when quite recent, a peculiar odor or *halitus*, which almost immediately disappears. An odor may, however,

afterwards be developed by addition of sulphuric acid, which is by some considered characteristic of the animal from which the blood was obtained.

Fig. 197.



The coagulation of blood in repose has been already noticed, and its cause traced to the mutual action of the fibrino-plastic and fibrino-genous substances, which together constitute fibrin: the effect is best seen when the blood is received in a shallow vessel, and left to itself some time. No evolution of gas or absorption of oxygen takes place in this process. By strong agitation coagulation may be prevented; the fibrin in this case separates in cohering filaments.

To the naked eye the blood appears a homogeneous fluid; but it is not so in reality. When examined by a good microscope, it is seen to consist of a transparent and nearly colorless liquid, in which float about a countless multitude of little round red bodies to which the color is due; these are the *blood-discs* or *blood-corpuscles* of microscopic observers. They are accompanied by colorless globules, fewer and larger, the *white corpuscles of the blood.*

The *blood-discs* are found to present different appearances in the blood of different animals: in the mammifers they look like little round red or yellowish discs, thin when compared with their diameter, being flattened or depressed on opposite sides. In birds, lizards, frogs, and fish, the corpuscles are elliptical. In magnitude they seem to be pretty constant in all the members of a species, but differ with the genus and order. In man they are very small, varying from $\frac{1}{6000}$ to $\frac{1}{3000}$ of an inch in breadth, while in the frog the long diameter of the ellipse measures at least four times as much. The corpuscles consist of an envelope containing a fluid in which the red coloring matter of the blood is dissolved.

The coagulation of blood effects a kind of natural proximate analysis; the clear, pale serum, or fluid part, is an alkaline solution of albumin, containing various soluble salts; the clot is a mechanical mixture of fibrin and blood-globules, swollen and distended with serum, of which it absorbs a large but variable quantity.

The following table represents the composition of healthy human blood as a whole; it is on the authority of M. Lecanu: *

	(1.)	(2.)
Water	780·15	785·58
Fibrin	2·10	3·57
Albumin	65·09	69·41
Coloring matter	133·00	119·63
Crystallizable fat	2·43	4·30
Fluid fat	1·31	2·27
Extractive matter of uncertain nature, soluble in both water and alcohol	1·79	1·92
Albumin in combination with soda	1·26	2·01
Sodium and potassium chlorides, carbonates, phosphates, and sulphates.	8·37	7·30
Calcium and magnesium carbonates; phosphates of calcium, magnesium, and iron; ferric oxide	2·10	1·42
Loss	2·40	2·59
	1000·00	1000·00

* Ann. Chim. Phys. xlviii. 320.

In healthy individuals of different sexes these proportions are found to vary: the fibrin and coloring matter are usually more abundant in the male than in the female: in disease, variations of a far wider extent are often apparent.

It appears singular that the red corpuscles, which are so easily dissolved by water, should remain uninjured in the fluid portion of the blood. This seems partly due to the presence of saline matter, and partly to that of albumin, the corpuscles being alike insoluble in a strong solution of salt and in a highly albuminous liquid. In the blood the limit of dilution within which the corpuscles retain their integrity appears to be nearly reached, for when water is added they immediately become attacked.

URINE. — The urine is the great channel by which the azotized matter of those portions of the body which have been taken up by the absorbents, and by which the excess of nitrogenous food is conveyed away and rejected from the system in the form of urea. It serves also to remove superfluous water and foreign soluble matters which get introduced into the blood.

The two most remarkable and characteristic constituents of urine, urea, and uric acid, have already been fully described; in addition to these, it contains lactic and hippuric acids, creatin, creatinine, and traces of glucose and indican, calcium and magnesium sulphates, chlorides, and phosphates, alkaline salts, and certain yet imperfectly known principles, including an odoriferous and a coloring substance.

Healthy human urine is a transparent, light amber-colored liquid, which, while warm, emits a peculiar, aromatic, and not disagreeable odor. This is lost on cooling, while the urine at the same time occasionally becomes turbid, from a deposition of urates, which redissolve with slight elevation of temperature. It is very decidedly acid to test-paper; this acidity, which continually varies in amount, has been ascribed to acid sodium phosphate, to free uric acid, and to free lactic acid; lactic acid can, however, hardly co-exist with alkaline urates, and the amorphous buff-colored deposit obtained from fresh urine by spontaneous evaporation in a vacuum, is not uric acid, but mixed acid urates, modified as to crystalline form by the presence of minute quantities of sodium chloride. That a free acid is sometimes present in the urine is certain: in this case the reaction to test-paper is far stronger, and the liquid deposits on standing, little, red, hard crystals of uric acid; but this is no longer a normal secretion.

An alkaline condition of the urine from fixed alkali is sometimes met with. Such alkalinity can always be induced by the administration of neutral potassium or sodium-salts of a vegetable acid, as tartaric or acetic acid: the acid of the salt is burned in the blood in the process of respiration, and a portion of the base appears in the urine in the state of carbonate. The urine is often alkaline in cases of retention, from ammonium carbonate produced by putrefaction in the bladder itself; but this is easily distinguished from alkalinity from fixed alkali, in which it is *secreted* in that condition.

The density of the urine varies from 1·005 to 1·030: about 1·020 to 1·025 may be taken as the average specific gravity. A high degree of density in urine may arise from an unusually large proportion of urea: in such a case, the addition of nitric acid will occasion an almost immediate production of crystals of urea nitrate; whereas with urine of the usual degree of concentration, very many hours will elapse before the nitrate begins to separate. The quantity of urine passed depends much upon circumstances, as upon the activity of the skin. It is usually more deficient in quantity and of higher density in summer than in winter. Perhaps about 32 ounces in the 24 hours may be assumed as a mean.

When kept at a moderate temperature, urine after some days begins to

decompose: it exhales an offensive odor, becomes alkaline from the production of ammonium carbonate, and turbid from the deposition of earthy phosphates. The ammonium carbonate is due to the putrefactive decomposition of the urea, which gradually disappears, the *ferment*, or active agent of the change, being a peculiar nitrogenous substance which is always voided with the urine. It has been found also that the yellow adhesive deposit containing infusoria from stale urine is a most powerful ferment to the fresh secretion. In this putrefied state urine is used in several of the arts, as in dyeing, and forms perhaps the most valuable manure for land known to exist.

Putrid urine always contains a considerable quantity of ammonium sulphide: this is formed by the deoxidation of sulphates by the organic matter. The highly offensive odor and extreme pungency of the decomposing liquid may be prevented by previously mixing the urine, as Liebig suggests, with sulphuric or hydrochloric acid, in sufficient quantity to saturate all the ammonia that can be formed.

The following is an analysis of human urine by Berzelius. 1000 parts contained—

Water	933·02
Urea	30·10
Lactates and extractive matter	17·14
Uric acid	1·00
Potassium and sodium sulphates	6·87
Sodium phosphate	2·92
Ammonium phosphate	1·65
Calcium and magnesium phosphates	1·00
Sodium chloride	4·45
Sal-ammoniac	1·50
Silica	0·03
Mucus of bladder	0·32
	1000·00

In certain states of disorder and disease, substances appear in the urine which are never present in the normal secretion: of these the most common is albumin. This is easily detected by the addition of nitric acid in excess, which then causes a white cloud or turbidity, which is permanent when boiled, or by corrosive sublimate, the urine being previously acidified with a little acetic acid; boiling usually causes a precipitate which is not dissolved by a drop or two of acid. Mere turbidity by boiling is no proof of albumin, the earthy phosphates being often thrown down from nearly neutral urine under such circumstances; the phosphatic precipitate is, however, instantly dissolved by a drop of any acid.

In *diabetes* the urine contains grape-sugar, the quantity of which varies with the intensity of the disease; sometimes it is enormous, the urine acquiring a density of 1·040 and beyond. It does not appear that the urea is deficient *absolutely*, although more difficult to discover from being mixed with such a mass of syrup. Very small traces of sugar may be discovered in urine by Trommer's test, formerly mentioned (p. 576): a few drops of solution of cupric sulphate are added to the urine, and afterwards an excess of caustic potash: if sugar be present, a deep blue liquid results, which, on boiling, deposits red cuprous oxide. With proper management this test is very valuable. Urine containing sugar, when mixed with a little yeast, and put in a warm place, readily undergoes vinous fermentation, and afterwards yields, on distillation, weak alcohol contaminated with ammonia.

The urine of children is said sometimes to contain benzoic acid: this is

produced by the decomposition of hippuric acid, which constantly occurs in the urine of healthy persons. When benzoic acid is taken, the urine after a few hours yields on concentration, and the addition of hydrochloric acid, needles of hippuric acid, soiled by adhering uric acid.

The deposit of buff-colored or pinkish amorphous sediment, which so frequently occurs in urine upon cooling, after unusual exercise or slight derangements of health, consists of a variable mixture of colored acid urates uncrystallized: it may be at once distinguished from a deposit of ammonio-magnesian phosphate by its instant disappearance on the application of heat. The earthy phosphates, besides, are hardly ever deposited from urine which has an acid reaction.

The coloring matters of the urine have been carefully examined by Dr. Schunck. He finds that most of the substances hitherto described as coloring healthy urine are products of the change of one, or at most two, coloring matters, which are always present. The first and most important of these, Dr. Schunck has obtained as a dark-yellow extract, amorphous and deliquescent, with a peculiar odor. It is soluble in alcohol and ether, as well as in water, and has the composition $C_{43}H_{51}NO_{26}$. It is decomposed at a boiling temperature, yielding a large quantity of a brown resin and volatile organic acid. A second extractive matter, soluble in water and alcohol, but not in ether, he found had the formula $C_{19}H_{27}NO_{14}$. This is certainly produced in the process of preparing the first extractive matter, and, perhaps, does not pre-exist in healthy urine. Heat and all strong alkalies and acids decompose these extractive matters, and give rise to most of the coloring matters which have hitherto been described as existing in healthy urine. The reddish-pink coloring matter, called purpurin or uro-erythrin, which adheres so tenaciously to the urates, is not an ordinary constituent of healthy urine, but is formed more especially when the secretion of bile is diminished. With regard to the presence of indican in healthy urine, see p. 583.

The yellow principle of bile may be observed in urine in cases of jaundice.

The urine of the carnivorous mammifera is small in quantity and highly acid. It has a very offensive odor, and quickly putrefies. In composition it resembles that of man, and is rich in urea. In birds and serpents, the urine is a white pasty substance, consisting almost entirely of urate of ammonia. In herbivorous animals it is alkaline and often turbid from earthy carbonates and phosphates: urea is still the characteristic ingredient, while of uric acid there is scarcely a trace: hippuric acid is usually, if not always, present, sometimes to a very large extent. When the urine putrefies, this hippuric acid, as already noticed, becomes changed to benzoic acid.

Urinary Calculi. — Stony concretions, differing much in physical characters and in chemical composition, are unhappily but too frequently formed in the bladder itself, and give rise to one of the most distressing complaints to which humanity is subject. Although many endeavors have been made to find some solvent or solvents for these calculi, and thus supersede the necessity of a formidable surgical operation for their removal, success has been but very partial and limited.

Urinary calculi are generally composed of concentric layers of crystalline or amorphous matter, of various degrees of hardness. Very frequently the central point or nucleus is a small foreign body: curious illustrations of this will be seen in any large collection. Calculi are not confined to man: the lower animals are subject to the same affliction; they have been found in horses, oxen, sheep, pigs, and almost constantly in rats.

The following is a sketch of the principal characters of the different varieties of calculi: —

1. *Uric Acid.* — These are among the most common: externally they are smooth or warty, of yellowish or brownish tint: they have an imperfectly crystalline, distinctly concentric structure, and are tolerably hard. Before the blowpipe the uric acid calculus burns away, leaving no ash. It is insoluble in water, but dissolves with facility in caustic potash, with but little ammoniacal odor: the solution mixed with acid gives a copious white curdy precipitate of uric acid, which speedily becomes dense and crystalline. Cautiously heated with nitric acid, and then mixed with a little ammonia, it gives the characteristic reaction of uric acid, viz., deep purple-red murexide.

2. *Ammonium Urate.* — Calculi of ammonium urate much resemble the preceding; they are easily distinguished, however. The powder boiled in water dissolves, and the solution gives a precipitate of uric acid when mixed with hydrochloric acid. It dissolves also in hot potassium carbonate with copious evolution of ammonia.

3. *Fusible Calculus; Calcium Phosphate with Ammonio-Magnesian Phosphate.* — This is one of the most common kinds. The stones are usually white or pale-colored, smooth, earthy, and soft; they often attain a large size. Before the blowpipe this substance blackens from animal matter, which calculi always contain; then becomes white, and melts to a bead with comparative facility. It is insoluble in caustic alkali, but readily soluble in dilute acids, and the solution is precipitated by ammonia. Calculi of unmixed calcium phosphate are rare, as also those of magnesium and ammonium phosphate; the latter salt is sometimes seen, forming small brilliant crystals, in cavities in the fusible calculus.

4. *Calcium Oxalate Calculus; Mulberry Calculus.* — The latter name is derived from the rough, warty character, and dark blood-stained aspect of this variety: it is perhaps the worst form of calculus. It is exceedingly hard: the layers are thick and imperfectly crystalline. Before the blowpipe the calcium oxalate burns to a carbonate by a moderate red heat, and, when the flame is strongly urged, to quicklime. It is soluble in moderately strong hydrochloric acid by heat, and very easily in nitric acid. When finely powdered and long boiled in a solution of potassium carbonate, potassium oxalate may be discovered in the filtered liquor when carefully neutralized by nitric acid, by white precipitates with solutions of lime, lead, and silver. A sediment of calcium oxalate in very minute, transparent, octohedral crystals, only to be seen by the microscope, is of common occurrence in urine, in which a tendency to deposits of urates exists.

5. *Cystine and Xanthine.* — These calculi are very rare, especially the latter. Calculi of cystine or cystic oxide are very crystalline, and often present a waxy appearance externally: sediments of cystic oxide are sometimes met with. This substance is a definite crystallizable organic principle, containing sulphur to a large amount, its formula being $C_3H_7NSO_2$. The powdered calculus dissolves in great part, without effervescence, in dilute acids and alkalies, including ammonia: the ammoniacal solution deposits, by spontaneous evaporation, small but beautiful colorless crystals, which have the form of six-sided prisms and tables. It forms a saline compound with hydrochloric acid. Caustic alkalies disengage ammonia from this substance by continued ebullition. When the solution in nitric acid is evaporated to dryness, it blackens: when it is dissolved in large quantity of caustic potash, a drop of solution of lead acetate added, and the whole boiled, a black precipitate containing lead sulphide makes its appearance. By these characters cystine is easily recognized.

Xanthine or *xanthic oxide*, also a definite organic principle, $C_5H_4N_4O_2$, is distinguished by the peculiar deep-yellow color produced when its solution in nitric acid is evaporated to dryness: it is soluble in alkalies and in boiling, strong hydrochloric acid.

Very many calculi are of a composite nature, the composition of the different layers being occasionally changed, or alternating: thus, mixed urates and calcium oxalate are not unfrequently associated in the same stone.

Sweat. — The watery fluid poured out by the skin contains from ½ to 2 per cent. of solid matter: the acidity of the secretion depends on organic acids, chiefly formic: acetic and butyric acids also exist in it. Lactic acid has been stated to be absent, even in rheumatism: a new acid named *sudoric acid*, and somewhat resembling uric acid in composition, is said to be always present. In disease, and in health, small quantities of urea also exist in sweat. The salts in the sweat are chlorides of sodium and potassium. Phosphoric acid, lime, magnesia, and iron oxide have been found.

Saliva is a mixture of several fluids secreted by different glands of the mouth. Its specific gravity is from 1·002 to 1·009. It is usually alkaline: during and after eating, the alkaline reaction increases, while it decreases by fasting. It contains an albuminous substance, *ptyalin*, which acts on starch, rapidly changing it into sugar. The secretion of the submaxillary gland, with the mucus of the mouth, chiefly produces this effect. On the passage of the food into the acid gastric juice, this conversion of starch into sugar ceases. The second remarkable substance in saliva is potassium sulphocyanate, which exists in very small quantities, but is very easily detected. The solid constituents of the saliva are about 1 per cent., and in 100 parts of solid constituents from 7 to 21 parts are fixed salts, chiefly chlorides, with calcium carbonate and phosphate.

Gastric Juice is a clear, colorless, transparent fluid, of sp. gr. 1·002, containing 1 to 2 per cent. of solid constituents, chiefly sodium chloride and lactate. It has an acid reaction, and contains hydrochloric, lactic, butyric, propionic, and acetic acids. It is slightly, or not at all, coagulable by boiling, though it contains two albuminous substances, one insoluble in water and absolute alcohol, the osmazome of older authors; the other soluble in water, but precipitated by alcohol, tannin, mercuric chloride, and lead-salts. This is pepsin. In the gastric juice of man it exists to the amount of 0·319 per cent. When the gastric juice has the greatest solvent power, 100 parts of fluid are saturated by 1·25 parts of potash. The gastric juice dissolves the albuminous substances taken as food, and slightly changes their reactions. Thus albumin, fibrin, casein, legumin, gluten, and chondrin give rise to as many different peptones. (See pepsin, p. 801.)

Bile. — This is a secretion of a very different character from the preceding: the largest internal organ of the body, the liver, is devoted to its preparation, which takes place from venous, instead of arterial blood. According to Gorup-Besanez, human bile contains in 1000 parts —

Water	823—908
Solid matter . . .	177— 92
Bile acids with alkali . .	108— 56
Fat and cholesterin . .	47— 40
Mucus and coloring matter	24— 15
Ash	11— 6

In its ordinary state, bile is a very deep-yellow, or greenish, viscid, transparent liquid, which darkens by exposure to the air, and undergoes changes which have been yet imperfectly studied. It has a disagreeable odor, a most nauseous, bitter taste, a distinctly alkaline reaction, and is miscible with water in all proportions. When evaporated to dryness at 100°, and treated with alcohol, the greater part dissolves, leaving behind an in-

soluble jelly of mucus of the gall-bladder. This alcoholic solution contains coloring matter and cholesterin: from the former it may be freed by digestion with animal charcoal, and from the latter by a large admixture of ether, in which the bile is insoluble, and separates as a thick, syrupy, and nearly colorless liquid. The coloring matter may also be precipitated by baryta-water.

Pure bile thus obtained, when evaporated to dryness by a gentle heat, forms a slightly yellowish brittle mass, resembling gum-arabic. It is completely soluble in water and absolute alcohol. The solution is not affected by the vegetable acids; hydrochloric and sulphuric acids, on the contrary, give rise to turbidity, either immediately or after a short interval. Lead acetate partly precipitates it; tribasic acetate precipitates it completely: the precipitate is readily soluble in acetic acid, in alcohol, and to a certain extent in excess of lead acetate. When carbonized by heat, and incinerated, bile leaves between 11 and 12 per cent. of ash, consisting chiefly of sodium carbonate, with a little common salt and alkaline phosphate. The beautiful researches of Strecker show that bile is essentially a mixture of the sodium-salts of two peculiar acids, resembling the resinous and fatty acids. One of these contains nitrogen, but no sulphur, and is termed *glycocholic acid*, being a conjugated compound * of a *non-nitrogenous acid*, *cholic acid*, with the azotized substance *glycocine* (p. 614); the other, containing nitrogen and sulphur, is called *taurocholic acid*, being a conjugated compound of the same *cholic acid* with a body to be presently described under the name of *taurin*, containing both nitrogen and sulphur. The relative proportion in which these acids occur in bile, remains pretty constant with the same animal, but varies considerably with different classes of animals.

Glycocholic Acid may be thus obtained:—When ox-bile is perfectly dried and extracted with cold absolute alcohol, and after filtration is mixed with ether, it first deposits a brownish tough resinous mass, and after some time, stellate crystals, consisting of the glycocholates of sodium and potassium. These mixed crystals were first obtained by Plattner, and they compose his so-called crystallized bile.

Glycocholic acid may be obtained by decomposing sodium glycocholate with sulphuric acid: it crystallizes in fine white needles of a bitterish-sweet taste, is soluble in water and alcohol, but only slightly in ether, and has a strong acid reaction. It is represented by the formula $C_{26}H_{43}NO_6$. When boiled with a solution of potash, the acid divides into cholic acid and glycocine:

$$\underset{\text{Glycocholic acid.}}{C_{26}H_{43}NO_6} + H_2O = \underset{\text{Cholic acid.}}{C_{24}H_{40}O_5} + \underset{\text{Glycocine.}}{C_2H_5NO_2}$$

Boiled with concentrated sulphuric or hydrochloric acid, it likewise yields glycocine, but instead of cholic acid, another white amorphous acid, *choloïdic acid* ($C_{24}H_{38}O_4$ = cholic acid minus 1 molecule of water), or, if the ebullition has continued for some time, a resinous substance, from its insolubility in water called *dyslysin* ($C_{24}H_{36}O_3$ = cholic acid minus 2 molecules of water).

Taurocholic Acid is thus procured: — Ox-bile is freed as far as possible from glycocholic acid by means of neutral lead acetate, and is then precipitated by basic lead acetate, to which a little ammonia is added. The precipitate is decomposed by sodium carbonate, whereby tolerably pure sodium taurocholate is obtained. By decomposing the taurocholate of lead with sulphuretted hydrogen, taurocholic acid is liberated. This sub-

* A compound is sometimes said to be "conjugated" of two others, when it contains the elements of those two bodies, minus the elements of water.

stance, however, which was previously called cholic acid and *bilin*, has never been obtained in the pure state; its formula, as inferred from the study of its products of decomposition, appears to be $C_{26}H_{45}NSO_7$. When boiled with alkalies, it divides into cholic acid and taurin:

$$\underset{\text{Taurocholic acid.}}{C_{26}H_{45}NSO_7} + H_2O = \underset{\text{Cholic acid.}}{C_{24}H_{40}O_5} + \underset{\text{Glycocine.}}{C_2H_7NSO_3}$$

With boiling acids it likewise gives taurin, but instead of cholic acid either choloïdic acid or dyslysin, according to the duration of the ebullition.

Taurin, $C_2H_7NSO_3$, crystallizes in colorless regular hexagonal prisms, which have no odor and very little taste. It is neutral to test-paper, and permanent in the air. When burnt, it gives rise to much sulphurous acid. It contains upwards of 25 per cent. of sulphur. It is easily prepared by boiling purified bile for some hours with hydrochloric acid. After filtration and evaporation, the acid residue is treated with five or six times its bulk of boiling alcohol, from which the taurin separates on cooling. Strecker made many attempts to prepare taurin artificially. Ultimately he found that when ammonium isethionate (p. 527), which melts at 130°, is heated to 210° or 220° C. (410°–428° F.), it loses 1 molecule of water, and becomes taurin. The substance is dissolved in water, and on the addition of alcohol, gives crystals having all the properties of taurin. Kolbe has recently observed the formation of taurin under very interesting circumstances. The treatment of potassium isethionate with phosphorus pentachloride gives rise to a heavy oily liquid, with simultaneous formation of hydrochloric acid and phosphorus oxychloride. This oily liquid, the so-called chloride of chlorethylsulphuric acid, $C_4H_4ClSO_2Cl$, when mixed with water, yields the corresponding acid, chlorethylsulphuric acid, $C_2H_5ClSO_3$, which on digestion with an excess of ammonia at 100°, produces taurin: $C_2H_5ClSO_3 + 2NH_3 = NH_4Cl + C_2H_7NSO_3$.

Cholic Acid, $C_{24}H_{40}O_5$, crystallizes in tetrahedrons. It is soluble in sulphuric acid, and on the addition of a drop of this acid and a solution of sugar (1 part of sugar to 4 parts of water), a purple-violet color is produced, which constitutes Pettenkofer's test for bile. At 195° C. (383° F.), it loses a molecule of water, and is converted into choloïdic acid, which change, as already pointed out, is also produced by ebullition with acids.

Cholic acid is best obtained by boiling the resinous mass precipitated by ether from the alcoholic solution of the bile, with a dilute solution of potash for 24 or 36 hours, till the amorphous potassium-salt that has separated begins to crystallize. When the dark-colored soft mass is removed from the alkaline liquid, dissolved in water, and hydrochloric acid added, a little ether causes the deposition of the cholic acid in crystals.

The principal coloring matter of the bile has been called *cholepyrrhin*. When dry it is reddish-brown and uncrystallizable, insoluble in water, more soluble in alcohol, which becomes yellow, and most soluble in caustic alkali. On the addition of nitric acid to the yellow alkaline solution, a change ensues. It passes through green, blue, violet, and red: after some time, it again turns yellow, probably in consequence of a gradual process of oxidation.

Another coloring matter has been called *biliverdin*. It is dark-green, amorphous without taste or smell, insoluble in water, slightly soluble in alcohol, but soluble in ether. Berzelius considers it to be identical with chlorophyl, the green coloring matter of leaves.

According to the researches of Strecker and Gundelach, pigs' bile differs from the bile of other animals. This bile contains an acid, to which the name of *glyco-hyocholic acid* has been given. It may be prepared in the following manner: fresh pigs' bile is mixed with a solution of sodium sul-

phate, and the precipitate obtained is dissolved in absolute alcohol, and decolorized by animal charcoal. From this solution ether throws down a sodium-salt, which on addition of sulphuric acid yields glyco-hyocholic acid as a resinous mass, which is dissolved in alcohol and re-precipitated by water.

Glyco-hyocholic acid contains $C_{27}H_{43}NO_5$. When heated with solutions of the alkalies, it undergoes a decomposition perfectly analogous to that of glycocholic acid, splitting up into glycocine and a crystalline acid, very soluble in alcohol, less so in ether, which has been termed *hyocholic acid.* This substance contains $C_{25}H_{40}O_4$; and the change is represented by the following equation:

$$\underset{\text{Glyco-hyocholic acid.}}{C_{27}H_{43}NO_5} + H_2O = \underset{\text{Hyocholic acid.}}{C_{25}H_{40}O_4} + \underset{\text{Glycocine.}}{C_2H_5NO_2}$$

When boiled with acids, glyco-hyocholic acid yields likewise glycocine, but instead of hyocholic acid, a substance representing the dyslysin of the ordinary bile, which might be termed *hyodyslysin.* The composition of hyodyslysin is $C_{25}H_{38}O_3$ = hyocholic acid minus H_2O.

Pigs' bile contains a very trifling quantity of sulphur, probably in the form of a sulphuretted acid corresponding to taurocholic acid of ox-bile. Strecker believes this acid to contain $C_{27}H_{45}NSO_6$: it might be called *tauro-hyocholic acid;* when boiled with an alkali, it should yield taurin and hyocholic acid. The sulphuretted acid must be present in pigs' bile in very minute quantity; it is even less known than taurocholic acid.

The once celebrated *oriental bazoar stones* are biliary calculi, said to be procured from a species of antelope: they have a brown tint, a concentric structure, and a waxy appearance, and consist essentially of a peculiar and definite crystallizable principle called *lithofellic acid.* To procure this substance, the calculi are reduced to powder and exhausted with boiling alcohol; the dark solution is decolorized by animal charcoal, and left to evaporate by gentle heat, whereupon the lithofellic acid is deposited in small, colorless, transparent six-sided prisms. It is insoluble in water, and sparingly soluble in ether, but dissolves with ease in alcohol: it melts at 94·5° C. (202° F.), and at a higher temperature burns with a smoky flame, leaving but little charcoal. Lithofellic acid dissolves without decomposition in concentrated acetic acid and in oil of vitriol: it forms a soluble salt with potash, and dissolves also in ammonia, but crystallizes out unchanged on evaporation. By analysis, lithofellic acid is found to consist of $C_{20}H_{36}O_4$.

The liver not only forms bile which is excreted, but it also effects a remarkable change in the blood that passes through it. M. Bernard discovered that after death, sugar could be detected in the blood from the hepatic vein, whilst no sugar was found in blood from the portal vein. In the progress of his researches into the origin of this sugar, he found that a *glycogenic substance* was formed in the substance of the liver itself, and this he succeeded in extracting and isolating (p. 594).

Pancreatic Fluid is strongly alkaline, and has a specific gravity of about 1·008 to 1·009, containing from 9 to 11 per cent. of solid constituents; among these are an albuminous substance resembling ptyalin, together with leucine, guanine, xanthine, and inosite, and about 1 per cent. of ash, chiefly chlorides and phosphates.

It has three distinct actions — first on starch, secondly on fat, and thirdly on albuminous matter. Starch is converted into sugar more energetically by the pancreatic fluid than by the saliva. Fat is changed into fatty acid and glycerin at a temperature of 35°; and boiled albumin and fibrin are

quickly dissolved at the same temperature, whilst the alkalescence distinctly remains.

Intestinal Juice is a colorless, alkaline fluid, containing from 3 to 4 per cent. of solid constituents. It is thought to be capable of dissolving fibrinous substances only.

Chyle.—The fluid of the lacteal vessels. This is a very variable fluid, milky, and feebly alkaline. Its fibrin begins to coagulate when taken from the vessels, in five to twelve minutes, and is perfectly coagulated in two to four hours. The coagulum is much smaller and weaker than that of the blood. That of the horse, from a yellowish color changes in the air to light red.

The albuminous saline serum contains very finely divided molecules, consisting of the minutest particles of fatty matter, which give rise to the milkiness; also larger chyle globules, and colorless blood globules. Thus the chyle approximates in composition and properties to the blood.

In the chyle of the horse there was found:

Water	91·00	to 96·00	per cent.
Fixed constituents	9·00	4·00	"
Nuclei and cells	Variable.		
Fibrin	0·19	0·7	"
Albumin	1·93	4·34	"
Fat	1·89	0·53	"
Extractive matter free from salts	7·27	8·34	"
Soluble salts	7·49	6·78	"
Insoluble about	2·00		

Lymph is the name given to the fluid in the lymphatic vessels. It is colorless, has an alkaline reaction, and coagulates in from four to twenty minutes. It closely resembles the blood without the blood globules. It contains colorless globules, resembling the white globules of the blood. It contains much less albumin and fat than the serum of the blood, but more water, and proportionately more extractive matter.

Closely resembling this fluid is that poured out by serous membranes and the cellular tissue. It has been called *exsudation fluid*, and may be divided into fibrinous and non-fibrinous. It may be considered as the serum of the blood with or without fibrin, which is far more commonly present than has been supposed.

Mucus and Pus.—The slimy matter effused upon the surface of various mucous membranes, as the lining of the alimentary canal, that of the bladder, of the nose, lungs, &c., to which the general name *mucus* is given, is so small in quantity, and so variable in consequence of any irritation of the membranes, that it is difficult to characterize. It always contains more or less epithelium and mucous cells. It contains a peculiar nitrogenous principle to which the name of *mucin* has been given (p. 800).

Pus, the natural secretion of a wounded or otherwise injured surface, is commonly a creamy, white, or yellowish liquid, which, under the microscope, appears to consist of multitudes of minute globules floating in a serum. It is neither acid nor alkaline.

The pus globules are distended by very dilute mineral and organic acids: imperfectly dissolved by alkalies, leaving the membrane of the cells adhering in a gelatinous mass. This cell membrane is an albuminous substance, soluble in very dilute acids. The pus serum contains more or less albumin, in all respects identical with that of the blood and a peculiar substance, *pyin* (p. 800).

The quantity of fatty substance is remarkable in pus, varying from 2 to

6 per cent. As much as 1 per cent. of cholesterin has been found to be present; but neither by this nor by any other character can the passage of mucus into pus be determined.

Milk.—The peculiar special secretion destined for the nourishment of the young is, so far as is known, very much the same in flesh-eating animals and in those which live exclusively on vegetable food. The proportions of the constituents may, however, sometimes differ to a considerable extent. The specific gravity varies from 1 018 to 1·045. It will be seen hereafter that the substances present in milk are wonderfully adapted to the office of providing materials for the rapid growth and development of the animal frame. It contains an azotized matter, casein or potassium albuminate, fatty principles, and a peculiar sugar, and lastly, various salts, among which may be mentioned calcium phosphate, held in complete solution in a slightly alkaline liquid. This last is especially important to a process then in activity, the formation of bone.

The white, and almost opaque, appearance of milk is an optical illusion: examined by a microscope of even moderate power, it is seen to consist of a perfectly transparent fluid, in which float about numbers of transparent globules: these consist of fat, surrounded by an albuminous envelope, which can be broken mechanically, as in the churning, or dissolved by the chemical action of caustic potash, after which, on agitating the milk with ether, the fat can be dissolved.

When milk is suffered to remain at rest some hours at the ordinary temperature of the air, a large proportion of the fat-globules collect at the surface into a layer of *cream;* if this be now removed and exposed for some time to strong agitation, the fat-globules coalesce into a mass, and the remaining watery liquid is expelled from between them and separated. The *butter* so produced must be thoroughly washed with cold water, to remove, as far as possible, the last traces of casein, which readily putrefies, and would in that case spoil the whole. A little salt is usually added.

Ordinary butter still, however, contains some butter-milk, and when intended for keeping should be *clarified*, as it is termed, by fusion. The watery part then subsides, and carries with it the residue of the azotized matter. The flavor is unfortunately somewhat impaired by this process. The consistence of butter, in other words, the proportions of solid fat and olein, is dependent upon the season, or more probably upon the kind of food; in summer the oily portion is always more considerable than in winter. The volatile odoriferous principle of butter, *butyrin*, has been already referred to.

The casein of milk, in the state of cheese, is in many countries an important article of food. The milk is usually heated to about 49° C. (120° F.), and coagulated by *rennet*, or an infusion of the stomach of the calf in water: the curd is carefully separated by a sieve from the whey, mixed with a due proportion of salt, and sometimes some coloring matter, and then subjected to strong and increasing pressure. The fresh cheese so prepared, being constantly kept cool and dry, undergoes a particular kind of putrefactive fermentation, very little understood, by which principles are generated which communicate a particular taste and odor. The goodness of cheese, as well as much of the difference of flavor perceptible in different samples, depends in great measure upon the manipulation: the best kinds contain a considerable quantity of fat, and are made with new milk: the inferior descriptions are made with skimmed milk.

Some of the Tartar tribes prepare a kind of spirit from milk by suffering it to ferment, with frequent agitation. The casein converts a part of the milk-sugar into lactic acid, and another part into grape-sugar, which in turn becomes converted into alcohol. Mare's milk is said to answer better for this purpose than that of the cow.

In a fresh state, and taken from a healthy animal, milk is always feebly alkaline. When left to itself, it very soon becomes acid, and is then found to contain lactic acid, which cannot be discovered in the fresh milk. The alkalinity is due to the soda which holds the casein in solution. In this soluble form casein possesses the power of taking up and retaining a very considerable quantity of calcium phosphate. The density of milk varies exceedingly: its quality usually bears an inverse ratio to its quantity. From an analysis of cow-milk in the fresh state by Haidlen,* the following statement of its composition in 1000 parts has been deduced:

Water	873·00
Butter	30·00
Casein	48·20
Milk-sugar	43·90
Calcium phosphate	2·31
Magnesium "	0·42
Iron "	0·07
Potassium chloride	1·44
Sodium "	0·24
Soda in combination with casein	0·42
	1000·00

Human milk is remarkable for the difficulty with which it coagulates: it generally contains a larger proportion of sugar than cow-milk, but scarcely differs in other respects.

* Annalen der Chemie und Pharmacie, xiv. 263.

ON THE ANIMAL TEXTURES.

NERVOUS SUBSTANCE; CONTRACTILE SUBSTANCE; ELASTIC TISSUE; SKIN.

NERVOUS SUBSTANCE. — The brain and nerves contain protagon (p. 803), cholesterin, and albuminous matter. In the watery extract are found creatin, uric acid, xanthine, sarcine, inosite, lactic acid; in the ash, sulphuric and phosphoric salts, especially potassium salts, a little sodium chloride, calcium and magnesium. The substance yields from 75 to 80 per cent. of water, and 3 to 4 of ash.

CONTRACTILE SUBSTANCE. — This, like nerve substance, consists of many different compounds. It contains 74 to 80 per cent. water, and 26 to 20 solid constituents. The most remarkable of these is syntonin, Liebig's fibrin of flesh (see p. 795). Casein, albumin, creatin, hypoxanthine, uric acid, and fat are also present. The solid constituents contain 4 to 5 per cent. of ash. Potash, soda, lime, magnesia, sulphuric, phosphoric, and hydrochloric acids are present.

ELASTIC TISSUE; SKIN. — The tendons and skin consist also of many different substances. Of these elastin (see p. 802) is one of the most remarkable. A cellular tissue, which yields gelatin when long boiled, is another constituent. These two principles combine with tannic acid, forming leather.

The principle of tanning, of such great practical value, is easily explained. When the skin of an animal, carefully deprived of hair, fat, and other impurities, is immersed in a dilute solution of tannic acid, the cellular and elastic tissues gradually combine with that substance as it penetrates inwards, forming a perfectly insoluble compound, which resists putrefaction completely: this is leather. In practice, lime-water is used for cleansing and preparing the skin, and an infusion of oak-bark, or sometimes catechu, or other astringent matter, as the source of tannic acid. The process itself is necessarily a slow one, as dilute solutions only can be safely used. Of late years, however, various contrivances, some of which show great ingenuity, have been adopted, with more or less success, for quickening the operation. All leather is not tanned: glove leather is dressed with alum and common salt, and afterwards treated with a preparation of the yolks of eggs, which contain an albuminous matter and a yellow oil. Leather of this kind still yields a size by the action of boiling water.

BONES. — At the age of 21 years the weight of the skeleton is to that of the whole body as 10·5 to 100 in man, and as 8·5 to 100 in woman, the weight of the body being about 125 or 130 lbs. Bones are constructed of organic matter called *ossein*, which yields gelatin on boiling, and is made stiff by insoluble earthy salts, of which calcium phosphate, $(PO_4)_2Ca''_3$, is the most abundant. The proportions of earthy and animal matter vary very much with the kind of bone and with the age of the individual, as

will be seen in the following table, in which the corresponding bones of an adult and of a still-born child are compared:

	Adult.		Child.	
	Inorganic matter.	Organic matter.	Inorganic matter.	Organic matter.
Femur . .	62·49	37·51	57·51	42·49
Humerus . .	63.02	36·98	58·08	41·92
Radius . .	60·51	39·49	56·50	43·50
Os temporum .	63·50	36·50	55·90	44·10
Costa . . .	57·49	42·51	53·75	46·25

The bones of the adult are constantly richer in earthy salts than those of the infant.

The following complete comparative analysis of human and ox bones is due to Berzelius:

	Human bones.	Ox bones.
Animal matter soluble by boiling . .	32·17	33·30
Vascular substance	1·13	
Calcium phosphate, with a little calcium fluoride	53·04	57·35
Calcium carbonate	11·30	3·85
Magnesium phosphate	1·16	2·05
Soda, and a little common salt . .	1·20	3·45
	100·00	100·00

The teeth have a very similar composition, but contain less organic matter: their texture is much more solid and compact. The enamel does not contain more than 2 or 3 per cent. of animal matter, whilst 81 to 88 per cent. of calcium phosphate with 7 or 8 per cent. of carbonate are present; and more calcium fluoride than in the bones.

ON CHEMICAL FUNCTIONS IN ANIMALS.

RESPIRATION, DIGESTION, NUTRITION.

RESPIRATION. — The simplest view that can be taken of a respiratory organ in an air-breathing animal, is that of a little membranous bag, saturated with moisture, and containing air, over the surface of which meander minute blood-vessels, whose contents, during the passage, are thus subjected to the chemical action of the air, through the substance of the membranes, and in virtue of the solubility of the gaseous matter itself in the water with which the membranes are imbued. In some of the lower classes of animals, where respiration is sluggish and inactive, these air-cells are few and larger; but in the higher kinds they are minute, and greatly multiplied in number, in order to gain extent of surface, each communicating with the external air by the windpipe and its ramifications.

Respiration is performed by the agency of the muscles which lie between and about the ribs, and by the diaphragm. In an ordinary respiration, from 22 to 43 cubic inches of air are thrown out. It has been said that as little as 3 and as much as 100 cubic inches have been expired. By a forced effort, ordinarily from 50 to 60 cubic inches are expelled, and after a full inspiration possibly from 100 to 300 cubic inches may be expired. Even then the lungs are not emptied of air. The residual quantity may be estimated at from 40 to 260 cubic inches. After an ordinary expiration a further quantity of air, amounting to from 77 to 170 cubic inches, may be expired, and after an ordinary inspiration, by the deepest sigh, from 119 to 200 more cubic inches may be drawn into the lungs. Usually about 15 respirations are made in a minute: the number, however, even in health, varies from 9 to 20.

The expired air is found to have undergone a remarkable change: it is loaded with aqueous vapor, while a very large proportion of oxygen has disappeared, and its place been supplied by carbon dioxide, air once breathed containing enough of that gas to extinguish a taper. The quantity of this gas is very liable to variation; usually from 3·3 to 6·2 per cent. of carbon dioxide is found to be present; when the respirations are few, the carbon dioxide is greatest, when many, least: thus with 6 respirations per minute, 5·5 per cent. has been found: with 48 respirations, 2·9 per cent. A full meal, cold weather, and increased barometric pressure, increase the carbon dioxide. Heat, alcohol, tea, and diminished pressure, lessen the carbon dioxide; age and sex produce definite effects. It appears most probable that nitrogen in small quantities is exhaled.

Whatever may be the difficulties attending the investigation of these subjects, — and difficulties there are, as the discrepant results of the experiments prove, — one thing is clear: namely, that quantities of hydrogen and carbon are daily oxidized in the body by the free oxygen of the atmosphere, and their products expelled from the system in the shape of water and carbon dioxide. Now, if it be true that the heat developed in the act of combination is a constant quantity, and no proposition appears more reasonable, part or all of the high temperature of the body must be the result of this exertion of chemical force.

The oxidation of combustible matter in the blood is effected in the capillaries of the whole body, not in the lungs, the temperature of which scarcely exceeds that of the other parts. The oxygen of the air is taken up in the lungs, and carried by the blood to the distant capillary vessels; by the aid of which, secretions, and all the mysterious functions of animal life, are undoubtedly performed: here the *combustion* takes place, although how this happens, and what the exact nature of the combustible may be, beyond the simple fact of its containing carbon and hydrogen, yet remains a matter of conjecture. The carbon dioxide produced is held in solution by the now venous blood, and probably confers, in great measure, upon the latter its dark color and deleterious action upon the nervous system. Once more poured into the heart, and by that organ driven into the second set of capillaries bathed with atmospheric air, this carbon dioxide is conveyed outwards, through the wet membrane, by a kind of *false diffusion*, constantly observed under such circumstances; while at the same time oxygen is, by similar means, carried inwards, and the blood resumes its bright-red color, and its capability of supporting life Much of this oxygen is, no doubt, simply dissolved in the serum. The hæmoglobin of the corpuscles, becoming oxyhæmoglobin in the arteries, acts as a carrier of another portion (p. 798). Mulder considers the fibrin to act in the same manner, being true fibrin in the veins, and, in part at least, oxidized in the arteries.

It would be very desirable to show, if possible, that the quantity of combustible matter daily burned in the body is adequate to the production of the heating effects observed. Something has been done with respect to the carbon. Comparison of the quantities and composition of the food consumed by an individual in a given time, and of the excretions, shows an excess of carbon in the former over the latter, amounting, in some cases, according to Liebig's high estimate,* to 14 ounces: the whole of which is thrown off in the state of carbon dioxide, from the lungs and skin, in the space of twenty-four hours. This statement applies to the case of healthy, vigorous men, much employed in the open air, and supplied with abundance of nutritious food. Females, and persons of weaker habits, who follow indoor pursuits in warm rooms, consume a much smaller quantity: their respiration is less energetic, and the heat generated less in amount. Those who inhabit very cold countries are well known to consume enormous quantities of food of a fatty nature, the carbon and hydrogen of which are, without doubt, chiefly employed in the production of animal heat. These people live by hunting: the muscular exertion required quickens and deepens the breathing; while, from the increased density of the air, a greater weight of oxygen is taken into the lungs, and absorbed into the blood at each inspiration. In this manner the temperature of the body is kept up, notwithstanding the piercing external cold: a most marvellous adjustment of the nature of the food, and even of the inclinations and appetite of the man, to the circumstances of his existence, enable him to bear with impunity an atmospheric temperature which would otherwise injure him.

The carbon consumed in respiration in one day, by a horse moderately fed, amounted, in a valuable experiment of M. Boussingault,† to 79 ounces; that consumed by a cow to 71 ounces. The determination was made in the manner just mentioned, viz., by comparing the quantity and composition of the food.

New and very important experiments on respiration have been made in Munich by Drs. Pettenkofer and Voit.

The apparatus was large enough to allow a man to breathe and move as in an ordinary dwelling-room for twenty-four hours at least. The air

* Animal Chemistry, p. 14.

† Annales de Chimie, vol. lxxi. pp. 136 and 137.

could be changed to the extent of from fifteen to seventy-five cubic meters an hour: the chemical difference between the air that went in and that which came out was determined.

The King of Bavaria gave about $3000 for the construction of the apparatus, and it acted so well that the quantity of carbon and of hydrogen in a stearin candle burnt in the apparatus could be determined as accurately by the quantity of carbon dioxide and water produced as by an organic analysis.

A dog and a man were experimented on. In the dog the amount of carbon dioxide expired was least after ten days of hunger; when a full diet of flesh and fat was taken, three times as much carbon dioxide was produced. The urea was increased twenty-two times as much as during starvation.

In man not quite one-third more carbon dioxide was produced when full diet was taken than was found during starvation.

From the amount of carbon dioxide and urea formed when animal food alone was taken, it appears that some fatty matter must be produced and retained in the system.

Starch and sugar diet do not appear to cause a deposit of fat directly, though they may do so indirectly.

Careful determination of the amount and composition of the food and oxygen consumed led to the belief that hydrogen and light carburetted hydrogen (CH_4) were given off in respiration. This is fully confirmed by these experiments. It follows from this important fact, first, that the carbon dioxide produced cannot be looked on as the measure of the amount of oxygen taken from the air, and secondly, that hydrogen cannot be assumed to be oxidized in the body in preference to carbon.

In a paper read to the Academy of Sciences at Munich, November, 1866, the authors give their latest results. They find that the proportion of carbon dioxide exhaled to oxygen inhaled is much greater in the day than in the night; with perfect rest day and night, nearly twice as much; with active motion during the day, nearly three times as much. The amount of oxygen taken in during rest by day is only half as much as is taken in at night, and after active motion the amount of oxygen taken in at night is still more. In diabetes the proportion of carbon dioxide exhaled by day to the oxygen inhaled is less than in health; at night the amount of oxygen inhaled may be less than half the amount that would be inhaled in health. When one-third of the blood consisted of white globules, the proportion of carbon dioxide exhaled to oxygen inhaled by day was much less than in health, and the amount of oxygen taken in at night was even less than is taken in during the day.

Digestion and Nutrition. — The various substances of which the food of man is composed must become finely divided in order to admit of their passage into the blood. In the process of fine division or solution different substances undergo different changes in the alimentary canal. We learn nothing by saying that the food is converted into chyme, and the chyme is changed into chyle; but each animal and vegetable substance must be considered separately, as regards the changes it undergoes when exposed to the action of the different fluids which constitute the saliva, gastric juice, bile, pancreatic juice, and intestinal fluid.

Shortly, it may be stated that mineral substances, when exposed to these reagents, are but little changed.

Hydrates of carbon, as cellulose, gum, starch, sugar, are each acted on differently by different secretions; thus cellulose and gum are probably not changed. Starch, by the action of the saliva and pancreatic fluid, becomes dextrin and glucose. Cane-sugar is changed by gastric juice and

heat into glucose, and all sugars are ultimately changed by the intestinal fluid and heat into acids.

Fat is unchanged by the saliva and gastric juice; but the bile, the pancreatic and intestinal fluid, change the fat into a finely divided emulsion, but effect no perfect solution.

Albuminous substances, as albumin, fibrin, casein, globulin, undergo subdivision and solution chiefly in the stomach. Each of these substances is chemically changed in the process of solution by the gastric juice (p. 797) into corresponding peptones. The rate of change and of solution depends on the mechanical subdivision as well as on the chemical properties of the different substances acted on.

Gelatinous substances are changed chemically by the gastric juice, and thereby lose the property of gelatinizing when cold. But this change is not requisite to their solution, which occurs so readily that these substances can often be taken as food when albuminous substances would remain in the stomach undissolved.

The constant and unceasing waste of the animal body in the process of respiration, and in the various secondary changes therewith connected, necessitates an equally constant repair and renewal of the whole frame by the deposition or organization of matter from the blood, which is thus gradually impoverished. To supply this deficiency of solid material in the circulating fluid is the office of the food. The striking contrast which at first appears in the nature of the food of the two great classes of animals, the vegetable feeders and the carnivorous races, diminishes greatly on close examination: it will be seen that, so far as the materials of blood, or, in other words, those devoted to the repair and sustenance of the body itself, are concerned, the process is the same. In a flesh-eating animal great simplicity is observed in the construction of the digestive organs; the stomach is a mere enlargement of the short and simple alimentary canal; and the reason is plain: the food of the creature, flesh, is absolutely identical in composition with its own blood, and with the body that blood is destined to nourish. In the stomach it undergoes mere solution, being brought into a state fitted for absorption by the lacteal vessels, by which it is nearly all taken up, and at once conveyed into the blood: the excrements of such animals are little more than the comminuted bones, feathers, hair, and other matters which refuse to dissolve in the stomach. The same condition, that the food employed for nourishment of the body must have the same, or nearly the same, chemical composition as the body itself, is really fulfilled in the case of animals that live exclusively on vegetable substances. It has been shown * that certain of the azotized principles of plants, which often abound, and are never altogether absent, have a chemical composition and assemblage of properties which assimilate them in the closest manner, and it is believed even identify them, with the azotized principles of the animal body: vegetable albumin, fibrin, and casein are scarcely to be distinguished from the bodies of the same name extracted from blood and milk.

If a portion of wheaten flour be made into a paste with water, and cautiously washed on a fine metallic sieve, or in a cloth, a grayish, adhesive, elastic, insoluble substance will be left, called *gluten* or *glutin*, and a milky liquid will pass through, which by a few hours' rest becomes clear by depositing a quantity of starch. If now this liquid be boiled, it becomes again turbid from the production of a flocculent precipitate, which, when collected, washed, dried, and purified from fat by boiling with ether, is found to have the same composition as animal albumin. The glutin itself is a mixture of true vegetable fibrin, and a small quantity of a peculiar azotized matter called *gliadin*, to which its adhesive properties are due.

* *Liebig*, Ann. Ch. Pharm. xxxix. 129.

The gliadin may be extracted by boiling alcohol, together with a thick, fluid oil, which is separable by ether: it is gluey and adhesive, quite insoluble in water, and when dry, hard and translucent like horn; it dissolves readily in dilute caustic alkali, and also in acetic acid. The fibrin of other grain is unaccompanied by gliadin: barley and oatmeal yield no glutin, but inadherent filaments of nearly pure fibrin.

Vegetable albumin in a soluble state abounds in the juice of many soft succulent plants used for food: it may be extracted from potatoes by macerating the sliced tubers in cold water containing a little sulphuric acid. It coagulates when heated to a temperature dependent upon the degree of concentration, and cannot be distinguished when in this state from boiled white of egg in a divided condition.

Almonds, peas, beans, and many of the oily seeds, contain a principle which bears the most striking resemblance to the casein of milk. When a solution of this substance is heated, no coagulation occurs, but a skin forms on the surface, just as with boiled milk. It is coagulable by alcohol, and by acetic acid, the last being a character of importance. Such a solution, mixed with a little sugar — an emulsion of sweet almonds, for instance — and left to itself, soon becomes sour and curdy, and exhales an offensive smell: it is then found to contain lactic acid.

All these substances dissolve in caustic potash, with production of a small quantity of alkaline sulphide: the filtered solution mixed with excess of acid gives precipitates of protein.

The following is the composition in 100 parts of vegetable albumin and fibrin: it will be seen that they agree very closely with the results before given:

	Albumin.	Fibrin.
Carbon	55·01	54·60
Hydrogen	7·23	7·30
Nitrogen	15·92	15·81
Oxygen, sulphur, and phosphorus	21·84	22·29
	100·00	100·00

The composition of vegetable casein, or *legumin*, has not been so well made out: so much discrepancy appears in the analyses as to lead to the supposition that different substances have been operated upon.

The great bulk, however, of the solid portion of the food of the herbivora consists of bodies which do not contain nitrogen, and therefore cannot yield sustenance in the manner described: some of these, as vegetable fibre or lignin, and waxy matter, pass unaltered through the alimentary canal; others, as starch, sugar, gum, and perhaps vegetable fat, are absorbed into the system, and afterwards disappear entirely: they are supposed to contribute very largely to the production of animal heat.

On these principles, Liebig* made the now doubtful distinction between what he terms *plastic elements of nutrition* and *elements of respiration.* In the former class he placed —

Vegetable fibrin,
Vegetable albumin,
Vegetable casein,
Animal flesh,
Blood.

To the latter:

Fat,	Grape-sugar,
Starch,	Milk-sugar,
Gum,	Pectin,
Cane-sugar,	Alcohol?

* Animal Chemistry, p. 96.

When the muscular movements of a healthy animal are restrained, a genial temperature kept up, and an ample supply of food containing much amylaceous or oily matter given, an accumulation of fat in the system rapidly takes place: this is well seen in the case of stall-fed cattle. On the other hand, when food is deficient, and much exercise is taken, emaciation results. These effects are ascribed to differences in the activity of the respiratory function: in the first instance, the heat-food is supplied faster than it is consumed, and hence accumulates in the form of fat; in the second, the conditions are reversed, and the creature is kept in a state of leanness by its rapid consumption. The fat of an animal appears to be a provision of Nature for the maintenance of life during a certain period under circumstances of privation.

The origin of fat in the animal body was at one time the subject of much discussion. On the one hand it was contended that satisfactory evidence exists of the conversion of starch and saccharine substances into fat, by separation of carbon and oxygen, the change somewhat resembling that of vinous fermentation; it was argued on the other side, that oily or fatty matter is invariably present in the food supplied to the domestic animals, and that this fat is merely absorbed and deposited in the body in a slightly modified state. The question has been decided in favor of the first of these views, which was enunciated by Liebig, by the very chemist who formerly advocated the second opinion. By a series of very beautiful experiments, MM. Dumas and Milne Edwards proved that bees exclusively feeding upon sugar were still capable of producing wax, which is known to be a veritable fat.

The food of animals, or rather that portion of the food which is destined to the repair and renewal of the frame itself, is thus seen to consist of substances identical in composition with the body it is to nourish, or requiring but little chemical change to become so.

The chemical phenomena observed in the animal system resemble so far those produced out of the body by artificial means, that they are all, or nearly all, so far as is known, changes in a descending series. Albumin and fibrin are probably more complex compounds than gelatin or the membrane which furnishes it: this, in turn, has a far greater complexity of constitution than urea, which contains most of the azotized matter that is rejected from the body. The animal lives by the assimilation into its own substance of the most complex and elaborate products of the organic kingdom; — products which are, and, apparently, can only be, formed under the influence of vegetable life.

The existence of the plant is maintained in a manner strikingly dissimilar: — the food supplied to vegetables is *wholly inorganic;* the carbon dioxide and nitrogen of the atmosphere; the water which falls as rain, or is deposited as dew; the minute traces of ammoniacal vapor present in the air; the alkali and saline matter extracted from the soil; — such are the substances which yield to plants the elements of their growth. That green healthy vegetables do possess, under circumstances to be mentioned immediately, the property of decomposing carbon dioxide absorbed by their leaves from the air, or conveyed thither in solution through the medium of their roots, is a fact positively proved by direct experiment, and rendered certain by considerations of a very stringent kind. To effect this very remarkable decomposition, the influence of light is indispensable; the diffused light of day suffices in some degree, but the direct rays of the sun greatly exalt the activity of the process. The carbon separated in this manner is retained in the plant in union with the elements of water, with which nitrogen is also sometimes associated, while the oxygen is thrown off into the air from the leaves in a pure and gaseous condition.

The effect of ammoniacal salts upon the growth of plants is so remark-

able as to leave little room for doubt concerning the peculiar functions of the ammonia discovered in the air. Plants which in their cultivated state contain, and consequently require, a larger supply of nitrogen, as wheat, and the cereals in general, are found to be greatly benefited by the application to the land of such substances as putrefied urine, which may be looked upon as a solution of ammonium carbonate, or of *guano*, which is the partially decomposed dung of birds, found in immense quantities on some of the barren islets of the western coast of South America, as that of Peru. More recently, similar deposits have been found on the coast of Southern Africa. The guano now imported into England from these localities is usually a soft, brown powder, of various shades of color. White specks of bone-earth, and sometimes masses of saline matter, may be found in it. That which is most recent, and probably most valuable as manure, often contains undecomposed uric acid, besides much ammonium oxalate or chloride, alkaline phosphates, and other salts: it has a most offensive odor. The specimens taken from older deposits have but little smell, are darker in color, contain no uric acid, and much less ammoniacal salt; the chief components are bone-earth, a peculiar dark-colored organic matter, and soluble inorganic salts. (See also p. 724).

Upon the members of the vegetable kingdom thus devolves the duty of building up, as it were, out of the inorganic constituents of the atmosphere, — the carbon dioxide, the water, and the ammonia, — the numerous complicated organic principles of the perfect plant, many of which are afterwards destined to become the food of animals, and of man. The chemistry of vegetable life is essentially a process of reduction caused by the action of light, but the mode in which this is effected is at present by no means made out. One thing, however, is manifest, namely, the wonderful relations between the two orders of organized beings, in virtue of which the rejected and refuse matter of the one is made to constitute the essential and indispensable food of the other. While the animal lives, it exhales incessantly from its lungs, and often from its skin, carbon dioxide; when it dies, the soft parts of the body undergo a series of chemical changes of *degradation*, which terminate in the production of carbon dioxide, water, ammonium carbonate, and, perhaps, other products in small quantity. These are taken up by a fresh generation of plants, which may in their turn serve for food to another race of animals.

APPENDIX.

HYDROMETER TABLES.

COMPARISON OF THE DEGREES OF BAUME'S HYDROMETER WITH THE REAL SPECIFIC GRAVITIES.

1. *For Liquids heavier than Water.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
0	1·000	26	1·206	52	1·520
1	1·007	27	1·216	53	1·535
2	1·013	28	1·225	54	1·551
3	1·020	29	1·235	55	1·567
4	1·027	30	1·245	56	1·583
5	1·034	31	1·256	57	1·600
6	1·041	32	1·267	58	1·617
7	1·048	33	1·277	59	1·634
8	1·056	34	1·288	60	1·652
9	1.063	35	1·299	61	1·670
10	1·070	36	1·310	62	1·689
11	1·078	37	1·321	63	1·708
12	1·085	38	1·333	64	1·727
13	1·094	39	1·345	65	1·747
14	1·101	40	1·357	66	1·767
15	1·109	41	1·369	67	1·788
16	1·118	42	1·381	68	1·809
17	1·126	43	1·395	69	1·831
18	1·134	44	1·407	70	1·854
19	1·143	45	1·420	71	1·877
20	1·152	46	1·434	72	1·900
21	1·160	47	1·448	73	1·944
22	1·169	48	1·462	74	1·949
23	1·178	49	1·476	75	1·974
24	1·188	50	1·490	76	2·000
25	1·197	51	1·495		

2. *Baumé's Hydrometer for Liquids lighter than Water.*

Degrees.	Specific Gravity.	Degrees.	Specific Gravity.	Degrees.	Specific Gravity.
10	1·000	27	0·896	44	0·811
11	0·993	28	0·890	45	0·807
12	0·986	29	0·885	46	0·802
13	0·980	30	0·880	47	0·798
14	0·973	31	0·874	48	0·794
15	0·967	32	0·869	49	0·789
16	0·960	33	0·864	50	0·785
17	0·954	34	0·859	51	0·781
18	0·948	35	0·854	52	0·777
19	0·942	36	0·849	53	0·773
20	0·936	37	0·844	54	0·768
21	0·930	38	0·839	55	0·764
22	0·924	39	0·834	56	0·760
23	0·918	40	0·830	57	0·757
24	0·913	41	0·825	58	0·753
25	0·907	42	0·820	59	0·749
26	0·901	43	0·816	60	0·745

These two tables are on the authority of Francœur; they are taken from the *Handwörterbuch der Chemie* of Liebig, Poggendorff, and Wöhler. Baumé's hydrometer is very commonly used on the Continent, especially for liquids heavier than water. For lighter liquids the hydrometer of Cartier is often employed in France. Cartier's degrees differ but little from those of Baumé.

In the United Kingdom, Twaddell's hydrometer is a good deal used for dense liquids. This instrument is so graduated that the real specific gravity can be deduced by an extremely simple method from the degree of the hydrometer; namely, by multiplying the latter by 5, and adding 1000; the sum is the specific gravity, water being 1000. Thus 10° Twaddle indicates a specific gravity of 1050, or 1·05; 90° Twaddell, 1450, or 1·45.

In the Customs and Excise, Sikes's hydrometer is used.

ABSTRACT

OF DR. DALTON'S TABLE OF THE ELASTIC FORCE OF VAPOUR OF WATER AT DIFFERENT TEMPERATURES, EXPRESSED IN INCHES OF MERCURY.

Temperature.		Force.	Temperature.		Force.	Temperature.		Force.
Fah.	Cent.		Fah.	Cent.		Fah.	Cent.	
32°	0°·0	0·200	57°	13°·88	0·474	90°	32°·2	1·36
33	0°·55	0·207	58	14°·4	0·490	95	35°	1·58
34	1°·1	0·214	59	15°	0·507	100	37°·77	1·86
35	1°·66	0·221	60	15°·5	0·524	105	40°·5	2·18
36	2°·2	0·229	61	16°·1	0·542	110	43°·3	2·53
37	2°·77	0·237	62	16°·66	0·560	115	46°·1	2·92
38	3°·3	0·245	63	17°·2	0·578	120	48°·88	3·33
39	3°·88	0·254	64	17°·77	0·597	125	51°·66	3·75
40	4°·4	0·263	65	18°·3	0·616	130	54°·4	4·34
41	5°	0·273	66	18°·88	0·635	135	57°·2	5·00
42	5°·55	0·283	67	19°·4	0·665	140	60°	5·74
43	6°·1	0·294	68	20°	0·676	145	62°·77	6·53
44	6°·66	0·305	69	20°·55	0·698	150	65°·5	7·42
45	7°·2	0·316	70	21°·1	0·721	160	71°·1	9·46
46	7°·77	0·328	71	21°·66	0·745	170	76°·66	12·13
47	8°·3	0·339	72	22°·2	0·770	180	82°·2	15·15
48	8°·88	0·351	73	22°·77	0·796	190	87°·77	19 00
49	9°·4	0·363	74	23°·3	0·823	200	93°·3	23·64
50	10°	0·375	75	23°·88	0·851	210	98°·88	28·84
51	10°·55	0·388	76	24°·4	0·880	212	100°	30·00
52	11°·1	0 401	77	25°	0·910	220	104°·4	34·99
53	11°·66	0·415	78	25°·5	0·940	230	110°	41·75
54	12°·2	0·429	79	26°·1	0·971	240	115°·5	49·67
55	12°·77	0·443	80	26°·66	1·000	250	121°·1	58·21
56	13°·3	0·458	85	29°·44	1·170	300	148°·88	111·81

TABLE

OF THE PROPORTION BY WEIGHT OF ABSOLUTE OR REAL ALCOHOL IN 100 PARTS OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES. (FOWNES.)

Sp. Gr. at 60° (15°·5C).	Per cent. of real Alcohol.	Sp. Gr. at 60° (15°·5C.)	Per cent. of real Alcohol.	Sp. Gr. at 60° (15°·5C).	Per cent. of real Alcohol.
0·9991	0·5	0·9511	34	0·8769	68
0·9981	1	0·9490	35	0·8745	69
0·9965	2	0·9470	36	0·8721	70
0·9947	3	0·9452	37	0·8696	71
0·9930	4	0·9434	38	0·8672	72
0·9914	5	0·9416	39	0·8649	73
0·9898	6	0·9396	40	0·8625	74
0·9884	7	0·9376	41	0·8603	75
0·9869	8	0·9356	42	0·8581	76
0·9855	9	0·9335	43	0·8557	77
0·9841	10	0·9314	44	0·8533	78
0·9828	11	0·9292	45	0·8508	79
0·9815	12	0·9270	46	0·8483	80
0·9802	13	0·9249	47	0·8459	81
0·9789	14	0·9228	48	0·8434	82
0·9778	15	0·9206	49	0·8408	83
0·9766	16	0·9184	50	0·8382	84
0·9753	17	0·9160	51	0·8357	85
0·9741	18	0·9135	52	0·8331	86
0·9728	19	0·9113	53	0·8305	87
0·9716	20	0·9090	54	0·8279	88
0·9704	21	0·9069	55	0·8254	89
0·9691	22	0·9047	56	0·8228	90
0·9678	23	0·9025	57	0·8199	91
0·9665	24	0·9001	58	0·8172	92
0·9652	25	0·8979	59	0·8145	93
0·9638	26	0·8956	60	0·8118	94
0·9623	27	0·8932	61	0·8089	95
0·9609	28	0·8908	62	0·8061	96
0·9593	29	0·8886	63	0·8031	97
0·9578	30	0·8863	64	0·8001	98
0·9560	31	0·8840	65	0·7969	99
0·9544	32	0·8816	66	0·7938	100
0·9528	33	0·8793	67		

TABLE

OF THE PROPORTION BY VOLUME OF ABSOLUTE OR REAL ALCOHOL IN 100 VOLUMES OF SPIRITS OF DIFFERENT SPECIFIC GRAVITIES (GAY-LUSSAC) AT 59° F. (15° C.)

100 vol. Spirits.		100 vol. Spirits.		100 vol. Spirits.	
Spec. Grav.	Contain vol. of real Alcohol.	Spec. Grav.	Contain vol. of real Alcohol	Spec. Grav.	Contain vol. of real Alcohol.
1·0000	0	0·9608	34	0·8956	68
0·9985	1	0·9594	35	0·8932	69
0·9970	2	0·9581	36	0·8907	70
0·9956	3	0·9567	37	0·8882	71
0·9942	4	0·9553	38	0·8857	72
0·9929	5	0·9538	39	0·8831	73
0·9916	6	0·9523	40	0·8805	74
0·9903	7	0·9507	41	0·8779	75
0·9891	8	0·9491	42	0·8753	76
0·9878	9	0·9474	43	0·8726	77
0·9867	10	0·9457	44	0·8699	78
0·9855	11	0·9440	45	0·8672	79
0·9844	12	0·9422	46	0·8645	80
0·9833	13	0·9404	47	0·8617	81
0·9822	14	0·9386	48	0·8589	82
0·9812	15	0·9367	49	0·8560	83
0 9802	16	0·0348	50	0·8531	84
0·9792	17	0·9329	51	0·8502	85
0·9782	18	0·9309	52	0·8472	86
0·9773	19	0·9289	53	0·8442	87
0·9763	20	0·9269	54	0·8411	88
0·9753	21	0·9248	55	0·8379	89
0·9742	22	0·9227	56	0·8346	90
0·9732	23	0·9206	57	0·8312	91
0·9721	24	0·9185	58	0 8278	92
0·9711	25	0·9163	59	0 8242	93
0·9700	26	0·9141	60	0·8206	94
0·9690	27	0·9119	61	0·8168	95
0·9679	28	0·9096	62	0·8128	96
0·9668	29	0·9073	63	0·8086	97
0·9657	30	0·9050	64	0·8042	98
0·9645	31	0·9027	65	0·8006	99
0·9633	32	0·9004	66	0·7947	100
0·9621	33	0·8980	67		

Source, . .	Vichy, France.	Ems, Nassau.	Selters, Nassau.	Karlsbrunnen, Silesia.	Karlsbad, Bohemia.
Name of Spring, .	Puits Carré.	Kessel-brunnen.	. .	. .	Sprudel.
Calcium	117·1	59 4	113·9	241·8	125·0
Barium	...	0·3	0·1	...	...
Strontium	1·7	0·6	1·4	...	0·5
Magnesium . . .	64·2	29·3	51·2	7·4	50·3
Sodium	1814·0	1122·9	1232·9	...	1793·0
Potassium . . .	162·7	34·7	47·8	...	...
Lithium	...	...	trace	...	...
Aluminium . . .	...	trace	trace	...	trace
Iron	2·0	1·6	trace	31·9	1·7
Manganese . . .	trace	0·2	trace	...	0·4
Chlorine	324·8	487·0	1388·5	14·1	630·2
Bromine	...	...	...	...	...
Iodine	...	...	...	...	...
Fluorine	...	0·1	1·5	...	1·5
Carbonic acid (CO_3) . .	2415·0	952·0	753·8	378·8	1028·5
Sulphuric acid (SO_4) .	196·8	38·7	28·4	39·6	1749·1
Nitric acid (NO_3) . .	...	...	...	...	0·4
Phosphoric acid (PO_4) .	16·7	...	0·4	...	0·4
Arsenic acid (AsO_4) . .	1·0	...	...	...	...
Silicic acid (SiO_3) . .	68·0	53·9	39·2	72·1	75·1
Sulphur	...	...	...	...	...
Organic Matter . .	...	...	...	...	...
Total solid constituents in 1,000,000 parts . .	5184·0	2780·7	3659·1	785·7	5456·1
Gaseous Constituents — in cubic centimetres per litre at 0° C. and 760 mm. bar.:					
Carbon dioxide . .	445	93	1087	406	1100
Nitrogen . . .	...	0·4	...	...	...
Ether	...	...	...	...	...
Hydrogen sulphide .	...	...	...	...	...
Temperature (Cent.) . .	43·75°	46°	15°	8°	74°
Specific gravity . .	...	1·0034	...	...	1·00497
Analysts . . .	Bouquet			Meissner	Berzelius

Püllna, Bohemia.	Seidschütz Bohemia.	Seidlitz, Bohemia.	Bath.	Cheltenham.	Harrowgate.	Wheal Clifford, Cornwall.	Saratoga.
..	Chief Spring.	Chief Spring.	King's Bath.	Royal Well.	Old Sulphur Well.	..	Congress.
139·6	385·8	722·9	386·7	179·5	493·6	1163·6	405·5
...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	6·6
3319·0	2813·7	2918·5	53·9	8·1	198·7	31·9	209·3
5222·0	1974·0	...	160·0	2701·4	4940·4	2042·2	2134·4
344·0	239·6	...	29·8	...	479·7	111.2	160 7
...	...	...	...	...	...	61·3	...
...	...	...	...	...	...		·6
...	and CO_3	...	7·4	4·1	...	traces	1·4
...	24·9	...	...	...	...		1·7
1913·3	211·1	292·0	265·3	2066·7	9187·4	5632·5	1505·6
...	trace	...	...	23·2	...	...	6·3
...	4·3	...	...	...	...	...	·2
...	...	...	...	...	...	...	...
...	463·7	904·0	86·9	639·5	104·8	...	...
656·2	14273·4	11568·6	1029·5	2259·1	18·2	123·8	1313·2
21154·0	2746·0	...	...	...	...	...	12·2
...	...	...	...	2·6	...	...	...
0·3	...	...	...	...	...	...	...
22·9	4·7	...	42·6	14·5	3·4	66·0	19·2
...	...	...	...	...	87·7	...	...
...	...	...	...	240·7	...	...	...
32771·3	23141·2	16406·0	2062·1	8139·4	15513·9	9232·5	5777·9
69	200	...	91·6	125	80·3	...	69·5
...	...	...	...	...	10·6	...	...
...	...	...	...	...	21·3	...	...
...	...	...	...	...	19·6	...	...
...	...	...	...	14°	9°	52°	10·
...	...	...	...	1·0064	1·01113	1·007	...
Struve	Berzelius	Naumann	Merck and Galloway	Abel and Rowney	Hofmann	Miller	Schweitzer

FRESH SPRING AND

Source, . . .	Spring at Whitley, Surrey.	Spring at Watford, Herts.	Artesian Well, Trafalgar Square.	Artesian Well, Guy's Hospital.	Artesian Well, Grenelle, Paris.
Calcium . . .	8·1	110·1	18·8	15·0	27·2
Magnesium . .	1·8	...	9·1	9·8	4·0
Sodium . . .	6·4	11·0	265·3	237·3	...
Potassium . .	2·3	...	99·0	7·8	23·8
Iron	...	...	...	...	...
Alumina and Ferric oxide . .	...	...	...	...	...
Chlorine . . .	12·8	12·1	174·2	139·3	5·2
Carbonic acid (CO_3)	trace.	156·0	197·1	134·4	60·5
Sulphuric acid (SO_4) .	13·3	6·8	180 5	158·4	6·6
Nitric acid (NO_3) .	...	19·0	...	...	...
Phosphoric acid (PO_4)	...	...	...	0·7	...
Silicic acid (SiO_3) .	12·3	11·6	13·1	11·3	6·0
Organic matter .	16·0	11·6	13·0	13·4	2 0
Total solid constituent in 1,000,000 parts. . .	73·0	338·2	970·1	727·4	135·3
Gaseous constituents, cub. cent. per litre:					
Carbon dioxide . .	trace.	...	30·4	0·7	1·5
Oxygen . . .	...	...	...	3·4	3·6
Nitrogen . . .	...	...	...	20·5	13·0
Temperature . .	...	...	14·5°	15·5°	28°
Specific gravity . .	...	...	1·00095	1·00077	...
Hardness . . .	2·8°	...	...	8°	...
Analysis . .	Graham, Miller, and Hofmann	Campbell	Abel and Rowney	Odling	Payen

OF

RIVER WATER.

St. Winifred's Holy Well, North Wales.	Thames, at Twickenham.	Thames, at Lambeth	Rhone, near Geneva.	Rhine, at Basle.	Ullswater Lake.	Loch Katrine.
115·9	83·8	69·4	45·3	55·5	8·3	1·9
11·0	4·7	6·0	2·7	4·8	1·8	0·8
13·6	9·2	11·1	3·1	0 6	5·4	...
trace	4·2	6·1	...	...	...	...
...	trace	...	3·9	...	...	...
...	trace	12·1	...	...	...	1 4
35·7	14·2	16·8	1·0	1 5	9·9	4·7
156·3	119·9	91·7	50·8	86·2	20·4	1·7
52·5	31·4	37·6	42·9	15·4	6·4	5·6
...	...	...	8·5	...	...	...
...	...	...	...	...	...	trace
39·1	3·9	14·9	23·8	2·1	3·0	0·1
...	49·7	37·0	...	3·3	5·0	11·4
424·1	321·0	302·7	182 0	169·4	60·2	27·6
81·8	5·1	63·2	8·4	...	1·8	0·3
...	...	...	8·0	...	7·5	9·3
...	...	...	18·4	...	15·5	18·4
11°	9·5°	...	...	...	...	...
1·001	1·0003	...	...	...	...	...
... 5	...	20·2	...	...	1·9	...
Barrat	Clark	Graham, Miller, and Hofmann	Deville	Pagenstecher	Way	Wallace

WEIGHTS AND MEASURES.

480·0 grains Troy = 1 oz. Troy.
437·5 " = 1 oz. Avoirdupoids.
7000·0 " = 1 lb. Avoirdupoids.
5760·0 " = 1 lb. Troy.

The imperial gallon contains of water at 60° (15°·5C) 70,000· grains.
The pint ($\frac{1}{8}$ of gallon)..... 8,750· "
The fluid-ounce ($\frac{1}{20}$ of pint)..... 437·5 "
The pint equals 34·66 cubic inches.

The French *kilogramme* = 15,433·6 grains, or 2·679 lb. Troy, or 2·205 lb. avoirdupoids.
The *grammme* = 15·4336 grains.
" *decigramme* = 1·5434 "
" *centigramme* = 0·1543 "
" *milligramme* = 0·0154 "

The *mètre* of France = 39·37 inches.
" *decimètre* = 3·937 "
" *centimètre* = 0·394 "
" *millimètre* = 0 0394 "

COMPARISON OF FRENCH AND ENGLISH MEASURES. By Dr. Warren De La Rue.

MEASURES OF LENGTH.

	In English Inches.	In English Feet = 12 Inches.	In English Yards = 3 Feet.	In English Fathoms = 6 Feet.	In English Miles = 1760 yards.
Millimètre	0·03937	0·0032809	0.0010936	0·0005468	0·0000006
Centimètre	0·39371	0·0328090	0·0109363	0·0054682	0·0000062
Décimètre	3·93708	0·3280899	0·1093633	0·0546816	0·0000621
Mètre	39·37079	3·2808992	1·0936331	0·5468165	0·0006214
Décamètre	393·70790	32·8089920	10·9363310	5·4681655	0·0062138
Hectomètre	3937·07900	328·0899200	109·3633100	54·6816550	0·0621382
Kilomètre	39370·79000	3280·8992000	1093·6331000	546·8165500	0·6213824
Myriomètre	393707·90000	32808·9920000	10936·3310000	5468·1655000	6·2138244

1 Inch = 2·539954 Centimètres.
1 Foot = 3·0479449 Décimètres.
1 Yard = 0·91438348 Mètre.
1 Mile = 1·6093149 Kilomètre.

MEASURES OF SURFACE.

	In English Square Feet.	In English Sq. Yards = 9 Square Feet.	In English Poles = 272·25 Sq. Feet.	In English Roods = 10,890 Sq. Feet.	In English Acres = 43,560 Sq. Feet.
Centiare or sq. mètre	10·7642993	1·1960333	0·0395383	0·000988457	0.0002471143
Are or 100 sq. mètres	1076·4299342	119·6033260	3·9538290	0·098845724	0·0247114310
Hectare or 10,000 sq. mètres	107642·9934183	11960·3326020	395·3828959	9·884572398	2·4711430996

1 Square Inch = 6·4513669 Square Centimètres.
1 Square Foot = 9·2899683 Square Décimetres.
1 Square Yard = 0·83609715 Square Mètre or Centiare.
1 Acre = 0·404671021 Hectare.

MEASURES OF CAPACITY.

	In Cubic Inches	In Cubic Feet = 1728 Cubic Inches.	In Pints = 34·65923 Cubic Inches.	In Gallons = 8 Pints = 277·27384 Cubic Inches.	In Busbels=8 Gallons = 2218·19075 Cubic Inches.
Millilitre, or cubic centimètre	0·061027	0·0000353	0·001761	0·00022010	0·000027512
Centilitre, or 10 cubic centimètres	0·610271	0·0003532	0·017608	0·00220097	0·000275121
Decilitre, or 100 cubic centimètres	6·102705	0·0035317	0·176077	0·02200967	0·002751208
Litre, or cubic décimètre	61·027052	0·0353166	1·760773	0·22009668	0·027512085
Decalitre, or centistère	610·270515	0·3531658	17·607734	2·20096677	0·275120846
Hectolitre, or decistère	6102·705152	3·5316581	176·077341	22·00966767	2·751208459
Kilolitre, or stère, or cubic mètre	61027·051519	35·3165807	1760·773414	220·09667675	27·512084594
Myriolitre, or decastère	610270·515194	353·1658074	17607·734140	2200·96676750	275·120845937

1 Cubic Inch = 16·3861759 Cubic Centimètres — 1 Cubic Foot = 28·3153119 Cubic Decimètres. — 1 Gallon = 4·543457969 Litres.

MEASURES OF WEIGHT.

	In English Grains.	In Troy Ounces = 480 Grains.	In Avoirdupois Lbs. = 7000 Grains.	In Cwts. = 112 Lbs. = 784,000 Grains.	Tons = 20 Cwts. = 15,680,000 Grains.
Milligramme	0·015432	0·000032	0·0000022	0·00000002	0·000000001
Centigramme	0·154323	0·000322	0·0000220	0·00000020	0·000000010
Decigramme	1·543235	0·003215	0·0002205	0·00000197	0·000000098
Gramme	15·432349	0·032151	0·0022046	0·00001968	0·000000984
Decagramme	154·323488	0·321507	0·0220462	0·00019684	0·000009842
Hectogramme	1543·234880	3·215073	0·2204621	0·00196841	0·000098421
Kilogramme	15432·348800	32·150727	2·2046213	0·01968412	0·000984206
Myriogramme	154323·488000	321·507267	22·0462126	0.19684118	0·009842059

1 Grain = 0·064798950 Gramme. — 1 Troy oz. = 31·103496 Gram. — 1 lb. Avd. = 0·45359265 Kilogr. — 1 Cwt. = 50·80237689 Kilog.

TABLE

FOR CONVERTING DEGREES OF THE CENTIGRADE THERMOMETER INTO DEGREES OF FAHRENHEIT'S SCALE.

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
—100° ...	—148·0°	—55° ...	— 67·0°	—10° ...	+14·0°
99 ...	146·2	54 ...	65·2	9 ...	15·8
98 ...	144·4	53 ...	63·4	8 ...	17·6
97 ...	142·6	52 ...	61·6	7 ...	19·4
96 ...	140·8	51 ...	59·8	6 ...	21·2
95 ...	139·0	50 ...	58·0	5 ...	23·0
94 ...	137·2	49 ...	56·2	4 ...	24·8
93 ...	135·4	48 ...	54·4	3 ...	26·6
92 ...	133·6	47 ...	52·6	2 ...	28·4
91 ...	131·8	46 ...	50·8	1 ...	30·2
90 ...	130·0	45 ...	49·9	0 ...	32·0
89 ...	128·2	44 ...	47·2	+1 ...	33·8
88 ...	126·4	43 ...	45·4	2 ...	35·6
87 ...	124·6	42 ...	43·6	3 ...	37·4
86 ...	122·8	41 ...	41·8	4 ...	39·2
85 ...	121·0	40 ...	40·0	5 ...	41·0
84 ...	119·2	39 ...	38·2	6 ...	42·8
83 ...	117·4	38 ...	36·4	7 ...	44·6
82 ...	115·6	37 ...	34·6	8 ...	46·4
81 ...	113·8	36 ...	32·8	9 ...	48·2
80 ...	112·0	35 ...	31·0	10 ...	50·0
79 ...	110·2	34 ...	29·2	11 ...	51·8
78 ...	108·4	33 ...	27·4	12 ...	53·6
77 ...	106·6	32 ...	25·6	13 ...	55·4
76 ...	104·8	31 ...	23·8	14 ...	57·2
75 ...	103·0	30 ...	22·0	15 ...	59·0
74 ...	101·2	29 ...	20·2	16 ...	60·8
73 ...	99·4	28 ...	18·4	17 ...	62·6
72 ...	97·6	27 ...	16·6	18 ...	64·4
71 ...	95·8	26 ...	14·8	19 ...	66·2
70 ...	94·0	25 ...	13·0	20 ...	68·0
69 ...	92·2	24 ...	11·2	21 ...	69·8
68 ...	90·4	23 ...	9·4	22 ...	71·6
67 ...	88·6	22 ...	7·6	23 ...	73·4
66 ...	86·8	21 ...	5·8	24 ...	75·2
65 ...	85·0	20 ...	4·0	25 ...	77·0
64 ...	83·2	19 ...	2·2	26 ...	78·8
63 ...	81·4	18 ...	0·4	27 ...	80·6
62 ...	79·6	17 ...	+1·4	28 ...	82·4
61 ...	77·8	16 ...	3·2	29 ...	84·2
60 ...	76·0	15 ...	5·0	30 ...	86·0
59 ...	74·2	14 ...	6·8	31 ...	87·8
58 ...	72·4	13 ...	8·6	32 ...	89·6
57 ...	70·6	12 ...	10·4	33 ...	91·4
56 ...	68·8	11 ...	12·2	34 ...	93·2

TABLE OF THERMOMETER SCALES (*continued*).

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
+35° ...	+95·0°	+85° ...	+185·0°	+135° ...	+275·0°
36 ...	96·8	86 ...	186·8	136 ...	276·8
37 ...	98·6	87 ...	188·6	137 ...	278·6
38 ...	100·4	88 ...	190·4	138 ...	280·2
39 ...	102·2	89 ...	192·2	139 ...	282·2
40 ...	104·0	90 ...	194·0	140 ...	284·0
41 ...	105·8	91 ...	195 8	141 ...	285·8
42 ...	107·6	92 ...	197·6	142 ...	287·6
43 ...	109·4	93 ...	199·4	143 ...	289·4
44 ...	111·2	94 ...	201·2	144 ...	291·2
45 ...	113·0	95 ...	203·0	145 ...	293·0
46 ...	114·8	96 ...	204·8	146 ...	294·8
47 ...	116·6	97 ...	206·6	147 ...	296·6
48 ...	118·4	98 ...	208·4	148 ...	298·4
49 ...	120·2	99 ...	210·2	149 ...	300·2
50 ...	122·0	100 ...	212·0	150 ...	302·0
51 ...	123·8	101 ...	213·8	151 ...	303·8
52 ...	125·6	102 ...	215·6	152 ...	305 6
53 ...	127·4	103 ...	217·4	153 ...	307·4
54 ...	129·2	104 ...	219·2	154 ...	309 2
55 ...	131·0	105 ...	221·0	155 ...	311·0
56 ...	132·8	106 ...	222·8	156 ...	312·8
57 ...	134·6	107 ...	224·6	157 ...	314·6
58 ...	136·4	108 ...	226·4	158 ...	316·4
59 ...	138·2	109 ...	228·2	159 ...	318·2
60 ...	140·0	110 ...	230·0	160 ...	320·0
61 ...	141·8	111 ...	231·8	161 ...	321·8
62 ...	143·6	112 ...	233·6	162 ...	323·6
63 ...	145·4	113 ...	235·4	163 ...	325·4
64 ...	147·2	114 ...	237·2	164 ...	327·2
65 ...	149·0	115 ...	239·0	165 ...	329·0
66 ...	150·8	116 ...	240·8	166 ...	330·8
67 ...	152·6	117 ...	242·6	167 ...	332·6
68 ...	154·4	118 ...	244·4	168 ...	334·4
69 ...	156·2	119 ...	246·2	169 ...	336·2
70 ...	158·0	120 ...	248·0	170 ...	338·0
71 ...	159·8	121 ...	249·8	171 ...	339·8
72 ...	161·6	122 ...	251·6	172 ...	341·6
73 ...	163·4	123 ...	253·4	173 ...	343·4
74 ...	165·2	124 ...	255·2	174 ...	345·2
75 ...	167·0	125 ...	257·0	175 ...	347·0
76 ...	168 8	126 ...	258·8	176 ...	348·8
77 ...	170·6	127 ...	260·6	177 ...	350 6
78 ...	172·4	128 ...	262·4	178 ...	352·4
79 ...	174·2	129 ...	264·2	179 ...	354·2
80 ...	176·0	130 ...	266·0	180 ...	356·0
81 ...	177·8	131 ...	267·8	181 ...	357·8
82 ...	179·6	132 ...	269·6	182 ...	359·6
83 ...	181·4	133 ...	271·4	183 ...	361·4
84 ...	183·2	134 ...	273·2	184 ...	363·2

TABLE OF THERMOMETER SCALES (*continued*).

Cent.		Fah.	Cent.		Fah.	Cent.		Fah.
+185°	...	+365·0°	+230°	...	+446·0°	+275°	...	+527·0°
186	...	366·8	231	...	447·8	276	...	528·8
187	...	368·6	232	...	449·6	277	...	530·6
188	...	370·4	233	...	451·4	278	...	532·4
189	...	372·2	234	...	453·2	279	...	534·2
190	...	374·0	235	...	455·0	280	...	536·0
191	...	375·8	236	...	456·8	281	...	537·8
192	...	377·6	237	...	458·6	282	...	539·6
193	...	379·4	238	...	460·4	283	...	541·4
194	...	381·2	239	...	462·2	284	...	543·2
195	...	383·0	240	...	464·0	285	...	545·0
196	...	384·8	241	...	465·8	286	...	546·8
197	...	386·6	242	...	467·6	287	...	548·6
198	...	388·4	243	...	469·4	288	...	550·4
199	...	390·1	244	...	471·2	289	...	552·2
200	...	392·0	245	...	473·0	290	...	554·0
201	...	393·8	246	...	474·8	291	...	555·8
202	...	395·6	247	...	476·6	292	...	557·6
203	...	397·4	248	...	478·4	293	...	559·4
204	...	399·2	249	...	480·2	294	...	561·2
205	...	401·0	250	...	482·0	295	...	563·0
206	...	402·8	251	...	483·8	296	...	564·8
207	...	404·6	252	...	485·6	297	...	566·6
208	...	406·4	253	...	487·4	298	...	568·4
209	...	408·2	254	...	489·2	299	...	570·2
210	...	410·0	255	...	491·0	300	...	572·0
211	...	411·8	256	...	492·8	301	...	573·8
212	...	413·6	257	...	494·6	302	...	575·6
213	...	415·4	258	...	496·4	303	...	577·4
214	...	417·2	259	...	498·2	304	...	579·2
215	...	419·0	260	...	500 0	305	...	581·0
216	...	420·8	261	...	501·8	306	...	582·8
217	...	422·6	262	...	503·6	307	...	584·6
218	...	424·0	263	...	505·4	308	...	586·4
219	...	426·2	264	...	507·2	309	...	588·2
220	...	428·0	265	...	509·0	310	...	590·0
221	...	429·8	266	...	510 8	311	...	591·8
222	...	431·6	267	...	512·6	312	...	593·6
223	...	433·4	268	...	514·4	313	...	595·4
224	...	435·2	269	...	516·2	314	...	597·2
225	...	437·0	270	...	518·0	315	...	599 0
226	...	438·8	271	...	519·8	316	...	600·8
227	...	440·6	272	...	521·6	317	...	602·6
228	...	442·4	273	...	523·4	318	...	604.4
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